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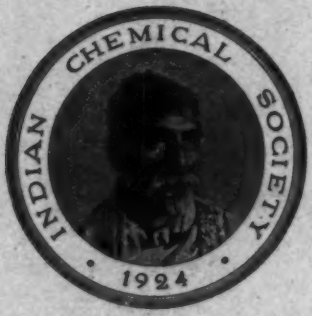

May, 1961

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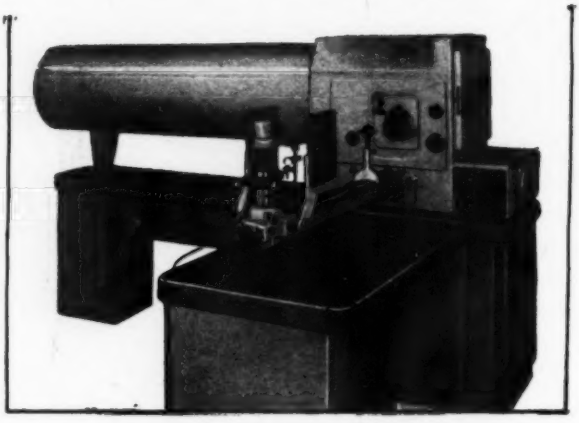

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MAY, 1961

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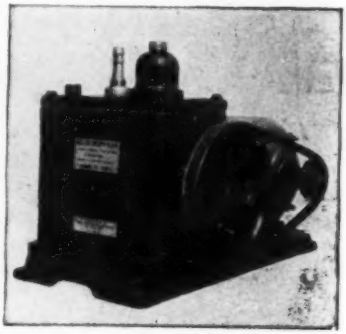

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[Jour. Indian Chem. Soc. Vol. 38, No. 5, 1961]

Leucoanthocyanidins and Related Compounds*

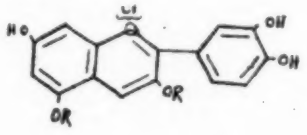
A. B. Kulkarni

To-day is the birth-anniversary of the late Dr. Basudev Banerjee in whose memory the Basudev Banerjee medal and prize are instituted. On behalf of myself and my research colleagues I pay homage to the memory of the late Dr. Basudev Banerjee. I am indeed grateful to the Council of the Indian Chemical Society for the award of the prize to me and calling upon me to deliver the second Basudev Banerjee Memorial Lecture.

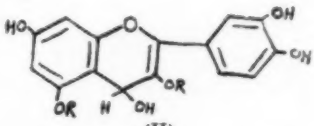
According to the conditions of award the lecture is to be based on the research work carried out during the last five years. Instead of giving diffuse and sketchy information on different topics I was interested in, during this period, I have confined myself to leucoanthocyanidins, which have recently aroused a great interest all over the World, and to which field my laboratory has made a substantial contribution.

Leucoanthocyanidins, their Occurrence in Nature and Importance

Anthocyanins, which are responsible for the red, violet, and blue pigmentations of flowers and many fruits, are derivatives of 2-benzopyrylium chloride (Ia). They give aglucones called, anthocyanidins (Ib) on hydrolysis with mineral acids. During the investigation of the young leaves of grape vine, Rosenheim[1] isolated a colorless substance, which yielded anthocyanidin on boiling with hydrochloric acid and called it as "leucoanthocyanin"[2]. He suggested that such compounds were glycosides (III) of the pseudobases (II) of the corresponding anthocyanidins.



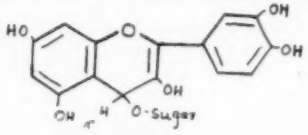
(I)



(II)

Cyanidin chloride. Ia: R=glucosyl. Ib: R=H, Cyanin pseudobase. R=glycosy, H.

Taking into consideration their relationship with anthocyanidins, they[3] preferred the term "leucoanthocyanidins" and proposed the structure (IV) for them. Later investigations on leucoanthocyanins led Robinson[4] to believe that these have the state of oxidation of dihydroanthocyanidins and hence are flavan-3,4-diols (V) rather than flavan-2,3,4-triols (IV).



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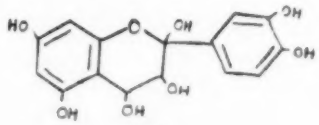
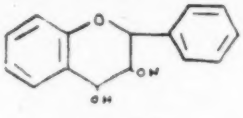


(IV)

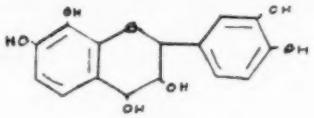
The isolation by King and Bottomley [5-6] of a naturally occurring flavan-3,4-diol-melaca-

*2nd Basudev Memorial Lecture, delivered under the auspices of the Indian Chemical Society at the Institute of Science, Bombay, on March 30, 1961.

cidin (VI) and its analogous behaviour towards mineral acids; the studies; of Bauer, Birch, and Hillis[7] on the reduction products of acetates of quercetin and aromadendrin indeed support the hypothesis of Robinson; now it may be safely concluded that the natural leucoanthocyanidins have a flavan-3,4-diol structure.



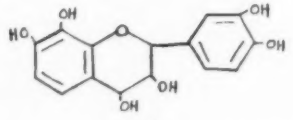
(VI)
A flavan-3,4-diol.



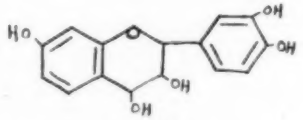
(V)
Melacacidin.

Leucoanthocyanins play a possible role in the biogenesis of flavonoid compounds. Robinson[2,4] suggested that the transformation of leucoanthocyanins into the colouring matters of the flavylium type might be occurring in nature. This concept that leucoanthocyanins are the immediate precursors of anthocyanins and flavonols, has been recently supported by several workers[8-17]. Two other interesting functions of leucoanthocyanins may be mentioned. Masquelier and Tayeau[18] have shown that the peanut leucoanthocyanin has vitamin-P activity and Audus[19] has reported stimulation of cell division by leucoanthocyanins.

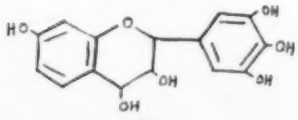
Robinson and Robinson[2] first showed the wide distribution of leucoanthocyanins in the plant kingdom. Bate-Smith and co-workers[20-25], however, pointed out that these were confined mainly to woody plants, and speculated a close structural relationship between leucoanthocyanins and the condensed tannins. This speculation has been amply supported during the last seven years and as many as eight representatives of this class of compounds have been isolated in crystalline form mostly from tannin-bearing plants. Melacacidin (VII) was discovered in *Acacia melanoxylon* by King and Bottomley[5,6]. Mollisacacidin (VIII) was isolated by Keppler[26] from *Acacia mollissima* and its enantiomorph was found in the quebracho wood by Freudenberg and co-workers[27-29]. This was followed by the isolation of leucorobinetinidin (IX) by Weinges[30] from *Robinia pseudacacia*. Seshadri and co-workers[31-33] reported the occurrence of leucocyanidin (X) in *Butea frondosa*, leucopelargonidin (XI) in *Eucalyptus calophylla* gum, and leucodelphinidin (XII) in *Cleistanthus collinus*. Very recently, presence of guibourtacacidin (XIII) in the specis of genus *Guibourtia* by Roux[34] and teracacidin (XIV) in *Acacia intertexta* by Clark-Lewis and Mortimer[35] is reported.



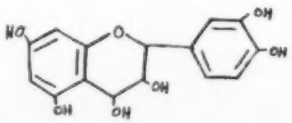
(VII)
7,8,3′,4′-Tetrahydroxyflavan-3,4-diol
(Melacacidin).



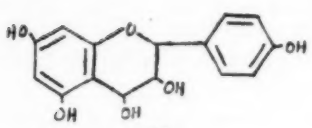
(VIII)
7,3′,4′-Trihydroxyflavan-3,4-diol
(Mollisacacidin).



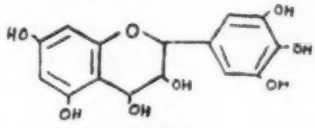
(IX)
7,3′,4′,5′-Tetrahydroxyflavan-3,4-diol
(Leucorobinetinidin).



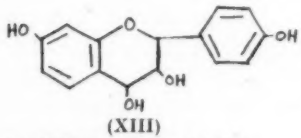
(X)
5,7,3′,4′-Tetrahydroxyflavan-3,4 diol
(Leucocyanidin).



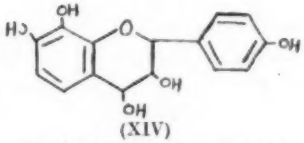
(XI)
5,7,4′,-Trihydroxyflavan-3,4-diol
(Leucopelargonidin).



(XII)
5,7,3′,4′,5′-Pentahydroxyflavan-3,4,diol
(Leucodelphinidin).

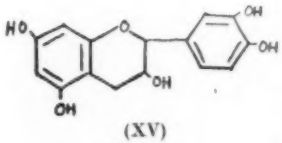


(XIII)
7,4′-Dihydroxyflavan-3,4-diol
(Guibourtacacidin).

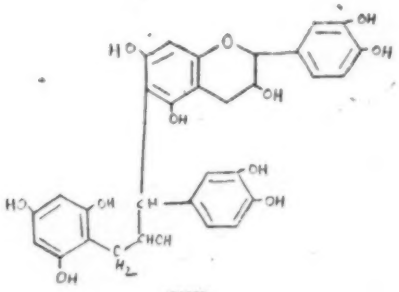


(XIV)
7,8,4′-Trihydroxyflavan-3,4-diol
(Teracacidin).

Until recently, very little was known about the structure of phlobatannins. In early twenties, **Freudenberg**[36] put forth his catechin hypothesis and stated that phlobatannins were the polymers of catechins. The following probable course of polymerisation with acidic reagents was suggested[37-38]. The present knowledge shows that catechins may be the building units of only a group of phlobatannins, which are present in Burma cutch or gambier extracts[39].

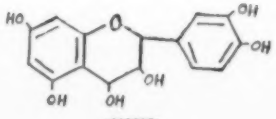


(XV)
Catechin.

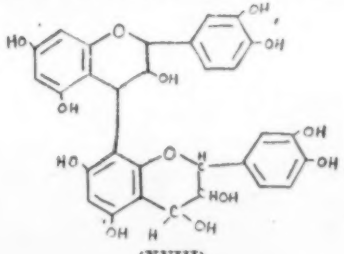


(XVI)
Dicatechin.

Like catechins, flavan-3,4-diols, themselves have no tanning properties; they are, however, polymerised with mineral acids to give soluble tannins and insoluble phlobaphenes[40-41]. Sufficient experimential evidence has been recently put forth by **Roux**[42-43] to show that this process of polymerisation takes place in the wood and monomeric leucoanthocyanidins



(XVII)
Leucocyanidin.



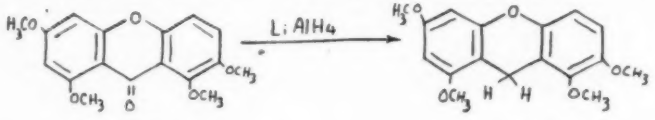
(XVIII)
Dileucocyanidin.

are converted into complex polymeric ones, which have tanning properties. Thus flavan-3,4-diols are the building units of at least a group of phlobatannins, which occur in wattle and quebracho wood[44]. A probable course of self-condensation[41] is indicated as shown above.

The above short review shows that leucoanthocyanidins are important as they themselves occur in nature, are the building units of phlobatannins, and play a significant role in the biogenesis of flavonoid pigments. Very little synthetic work has been reported in the field and hence studies in that direction are essential. The problem of synthesis of flavan-3,4-diols is exciting and complicated because of the three asymmetric centres present in the molecule. Four racemates or eight optically active isomers of an individual flavan-3,4-diol are theoretically possible and are likely to occur in nature. An elaborate programme of research on different aspects of leucoanthocyanidins was therefore undertaken with my colleagues at the National Chemical Laboratories, Poona and the Institute of Science, Bombay. Methods for their synthesis were evolved, their stereochemistry was established, and a few naturally occurring ones were synthesised.

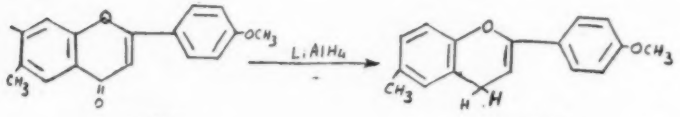
Synthesis of the Four Racemates of 6-*Methyl*-4′-*methoxyflavan*-3,4-*diol*

Preliminary investigations on the reduction of anthoxanthins, such as, 1,2,6,8-tetramethoxyxanthone (XIX), 6-methyl-4′-methoxyflavone (XX), 6-methyl-3, 4′-dimethoxyflavone (XXI), and 6-methyl-4′-methoxyflavanone (XXII), with lithium aluminium hydride were carried out with a view to studying the course of reduction and to establishing the optimum experimental conditions. The corresponding xanthene[46] (XXIII),



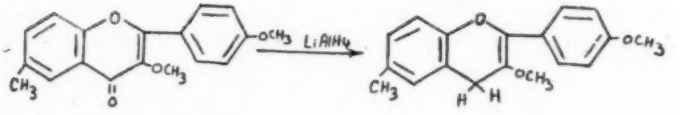
(XIX)
1,2,6,8-Tetramethoxyxanthone.

(XXIII)
1,2,6,8-Tetramethoxyxanthene.



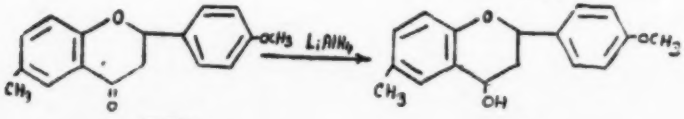
(XX)
6-Methyl-4′-methoxyflavone.

(XXIV)
6-Methyl-4′-Methoxyflav-2-ene.



(XXI)
6-Methyl-3,4′-dimethoxyflavone.

(XXV)
6-Methyl-3,4′-dimethoxyflav-2-ene.

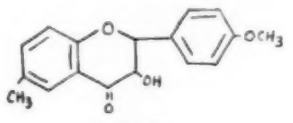


(XXII)
6-Methyl-4′-methoxyflavanone.

(XXVI)
6-Methyl-4′-metyhoxyflavan-4-ol.

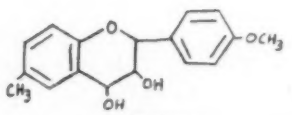
flavene[46] (XXIV), 3-methoxyflav-2-ene[47] (XXV), and flavan-4-ol[47] (XXVI) were obtained respectively. In the case of reduction of the flavanone, only one isomer could be obtained though theoretically two can exist.

The First Two Racemates.—Thus it has been established that metal hydrides are convenient reducing agents for anthoxanthins. It was thought that the dihydroflavonols would serve as intermediates and would give the desired leucoanthocyanidins on reduction with these reagents. When these investigations were undertaken in 1954, a survey of the literature showed that only an isolated example of synthetic flavan-3, 4-diol, *i.e.*, the unsubstituted one[48] was known. 6-Methyl-4′-methoxydihydroflavonol (XXVII) was therefore reduced with lithium aluminium hydride and the corresponding two flavan-3, 4-diols[49,50] (XXVIII and XXIX), isomeric in position '4', were isolated. Almost simultaneously, publications from Freudenberg and Roux[51], King and Clark-Lewis[52-53], and Swain[54] appeared wherein they reported the synthesis of flavandiols. Only one racemate in each case was, however, reported by these workers.

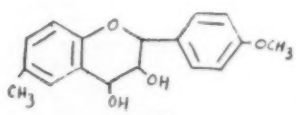


(XXVII)
6-Methyl-4′-methoxydihydroflavonol

| $LiAlH_4$



(XXVIII)
6-Methyl-4′-methoxyflavan-3,4-diol (m.p. 160°).



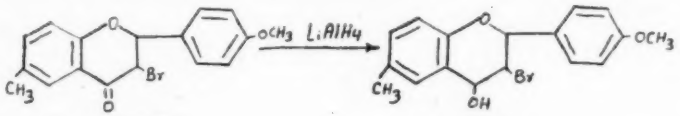
(XXIX)
6-Methyl-4′-methoxyflavan-3,4-diol, (m.p. 193°).

The Third Racemate.—Having accomplished the synthesis of the first two racemates, we directed our attention to the synthesis of the remaining two racemates. The obvious choice of the starting material would be the corresponding isomeric dihydroflavonol having a different configuration for the C_3-OH. We were therefore dragged into the field of dihydroflavonols—different methods for their synthesis and their stereochemistry. These investigations form a separate chapter in itself and are discussed in the later part of the lecture. It is relevant to note here that the isomeric dihydroflavonol could not be synthesised[55,56] and the approach had to be reluctantly abandoned. Attempts to use the flav-3-ene as an intermediate for the synthesis of a flavan-3, 4-diol through the following sequence of reactions also failed[57].

Flavan-4-ol $\xrightarrow{-H_2O}$ Flav-3-ene $\xrightarrow{\text{per acid}}$ Flavan-2,4-epoxide $\xrightarrow{\text{dilute acid}}$ Flavan 3,4-diol.

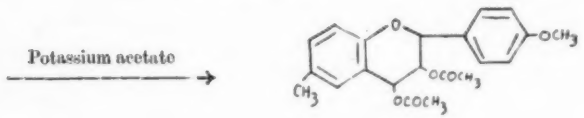
At this stage of the investigation a stray observation of Limaye[58] that 6-methyl-4′-methoxy-3-bromoflavanone exists in two isomeric forms, became useful to us. Both these isomers of 6-methyl-4′-methoxy-3-bromoflavanone were synthesised and their isomerism in position '2' was proved[55] by the fact that on dehydrobromination both gave the same corresponding flavone. Replacement of bromine of both the compounds by a hydroxy or an acetoxy group and synthesis of the isomeric dihydroflavonols could not be realised as

dehydrobromination to the corresponding flavone occurred[55]. This difficulty was circumvented by first reducing the bromoflavanones to the bromohydrins with lithium aluminium hydride. 6-Methyl-4′-methoxy-3-bromoflavanone (XXX) was reduced with lithium aluminium hydride to the bromohydrin (XXXI) and bromine was replaced by a hydroxy group by boiling the bromohydrin with alkali in dioxan[59]. Thus the third racemate of 6-methyl-4′-methoxyflavan-3,4-diol was synthesised. Its diacetate (XXXII) could be obtained in a crystalline form from the diol by acetylation or directly by treating the bromohydrin with anhydrous potassium acetate. Repetition of the experimental conditions on the isomeric 3-bromoflavanone (XXXIII) gave the bromohydrin (XXXIV); replacement of bromine by a hydroxy or an acetoxy group was, however, unsuccessful and resulted, presumably, in the formation of 6-methyl-4′-methoxyflav-3-ene-4-acetate[59] (XXXV). Attempts to prepare the flavan-3, 4-epoxide from this bromohydrin with a view to opening it stereospecifically to the flavan-3, 4-diol also failed[59].

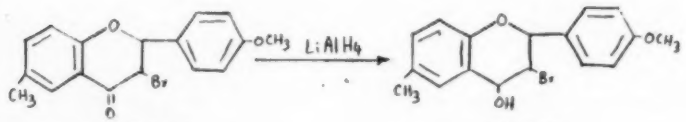


(XXX)
6-Methyl-4′-methoxy-3-bromoflavanone (m.p. 138°).

(XXXI)
6-Methyl-4′-methoxy-3-bromoflavanol 4-ol (m.p.200°).

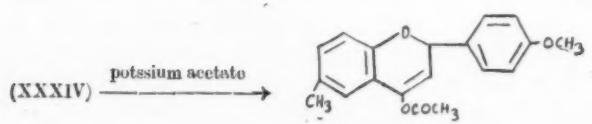


(XXXII)
6-Methyl-4′-methoxyflavan-3,4-diol diacetate, (m.p. 150°).



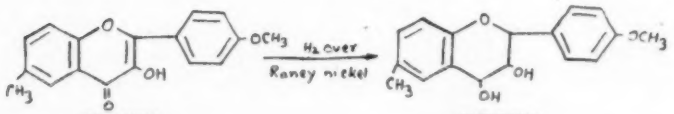
(XXXIII)
6-Methyl-4′-methoxy-3-bromoflavanone (m.p. 167°).

(XXXIV)
6-Methyl-4′-methoxy-3-bromoflavan-4-ol (m.p. 175)°.



(XXXV)
6-Methyl-4′-methoxyflav-3-ene-4-acetate.

The Fourth Racemate.—By this time, stereochemical investigations on flavan-3, 4-diols in our laboratory and elsewhere were sufficiently advanced to give us a clue that the fourth racemate of 6-methyl-4′-methoxyflavan-3, 4-diol could be synthesised by catalytic hydrogenation of the corresponding flavonol. 6-Methyl-4′-methoxyflavonol (XXXVI) was hydrogenated over Raney nickel at high temperature and pressure, and, indeed, the corresponding flavan-3, 4-diol (XXXVII), the fourth racemate, was obtained[56'60].



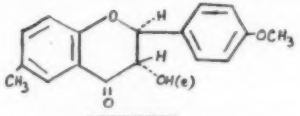
(XXXVI)
6-Methyl-4′-methoxyflavonol
(m.p. 192°).

(XXXVII)
6-Methyl-4′-methoxyflavan-3-4-diol
(m.p. 162°).

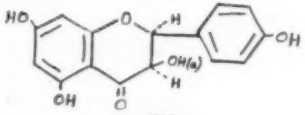
Stereochemistry of Leucoanthocyanidins

The above synthetic work on leucoanthocyanidins would not be complete unless their stereochemistry was established. As very little stereochemical data on the intermediate compounds, such as, dihydroflavonols, bromoflavanones, and bromohydrins, were known, detailed stereochemical investigations on these compounds were carried out and the stereochemistry of leucoanthocyanidins was settled.

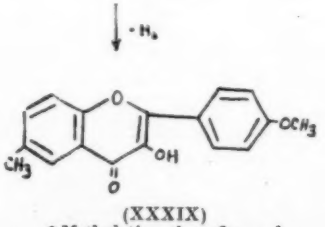
Stereochemistry of Dihydroflavonols.—A dihydroflavonol contains two asymmetric centres and hence can exist in two racemic forms. We were the first to introduce Barton's concept of conformational analysis[61] in this field to elucidate its stereochemistry[62]. The dihydropyran ring was compared with cyclohexene[63] and the bulky side phenyl nucleus was assigned an equatorial conformation[55,62]. On the basis of dehydrogenation data[55] on some of the dihydroflavonols, synthesised in our laboratory, along with that put forth by Seshadri and co-workers[64] on natural and synthetic 3-hydroxynaringenin, an equatorial conformation for C_3-OH of the synthetic dihydroflavonols was proposed. Thus a working hypothesis[55] has been put forward that C_2-phenyl and C_3-OH of the synthetic dihydroflavonols, which are dehydrogenated, are *trans*-oriented. The dehydration between C_2-H and C_3-OH of 3-hydroxynaringenin, which was prepared by a replacement reaction, was explained[55] on the basis of *trans*-(a, a) elimination principle[61]. It was therefore assigned a *cis*-configuration [C_2-Ph(e), C_3-OH(a)]. Seshadri and co-workers[65] arrived at the same conclusions regarding the stereochemistry of dihydroflavonols.



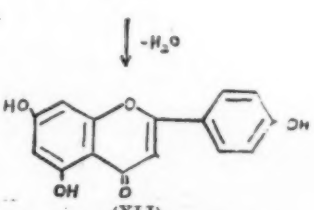
(XXXVIII)
trans-6-Methyl-4′-methoxydihydroflavonol.



(XI)
cis-5, 7, 4′-Trihydroxydihydroflavonol
(3-hydroxynaringenin from naringenin by oxidation).



(XXXIX)
6-Methyl-4′-methoxyflavonol.



(XLI)
5,7,4′-Trihydroxyflavone.

It became necessary to prove to which series the dihydroflavonols synthesised by different methods belonged and, if possible, to prepare an epimeric dihydroflavonol with C_3-OH(a) so that it might serve as an intermediate for the synthesis of the third and the fourth race-

mates. All the methods for the synthesis of dihydroflavonols were therefore worked out in our laboratory ; the identical dihydroflavonols were synthesised by two different methods and thus the various methods were correlated. An epimeric (±)-6-methyl-4′-methoxy-dihydroflavonol, required for the synthesis of the third and the fourth racemate, could not be synthesised by any of the known methods. The established co-ordination among the methods of synthesis and the dehydrogenation data on the dihydroflavonols enabled us, however, to assign conformations to both the synthetic and natural dihydroflavonols. The results are tabulated below.

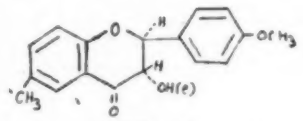
TABLE I

Conformations of synthetic and natural dihydroflavonols[55].

Dihydroflavonol.	Nature.	Dehydrogenation or dehydration with H_2SO_4.	Conformation for C_3-OH.
1st Series:			
1. 6-Methyl-4′-methoxy	Synthetic	Dehydrogenation	e
2. 7,4′-Dimethoxy	,,	Not known	e
3. 7,8,3′,4′-Tetramethoxy	,,	Dehydrogenation	e
4. 6-Benzoyl-4′-methoxy	,,	Not known	e
5. Fustin trimethyl ether	,,	,,	e
6. Taxifolin	Natural	Dehydrogenation	e
7. Dihydrorobinetin	,,	,,	e
8. 3-Hydroxynaringenin	,,	,,	e
9. Alpinone	,,	Not known	e
,,	Synthetic		
10. Pinobanksin	Natural converted to alpinone	No dehydrogenation (?)	e
2nd Series:			
11. 3-Hydroxynaringenin	Synthetic	Dehydration	a
12. 3-Hydroxyhesperitin	,,	Not known	a

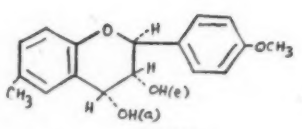
As the table reveals, we proposed that the naturally occurring dihydroflavonols belong to the *trans*-series[55]. The validity of this hypothesis, that the naturally occurring dihydroflavonols are *trans* compounds, is established beyond doubt by later publications of Freudenberg and Weinges[29] and Clark-Lewis and co-workers[66]. Thus (±)-dihydroquercetin tetramethyl ether was converted by hydrogenation over platinum catalyst to (±)-catechin tetramethyl ether[67], the stereochemistry of which as 2, 3-*trans*-compound is well established.

Stereochemistry of the First Two Racemates.—Thus the synthetic 6-methyl-4′-methoxy-dihydroflavonol (XLII) was assigned a *trans*-configuration [C_2-Ph(e) ; C_3-OH(e)] and hence the stereochemistry of the first two racemates of 6-methyl-4′-methoxyflavan-3, 4-diol could be deduced. On the basis of the generalisation[61] that catalytic hydrogenation of an unhindered ketone in an acidic medium affords an axial alcohol, C_4—OH of the lower melting racemate was assigned an axial conformation. It followed that C_4-OH of the other isomer was equatorial. Thus the lower melting racemate (XLIII) was assigned 2,3-*trans*-3,4-*cis*-configuration [C_2-Ph(e), C_3-OH(e), C_4-OH(a)] and the higher melting isomer (XLIV) 2, 3-*trans*-3, 4-*trans*-configuration[62-68] [C_2-Ph(e), C_3-OH(e), C_4-OH(e)]. The assignments postulated comply with Auwer-Skita rule[69] and are further supported by the fact that only the isomer having 3, 4-*cis*-configuration [C_3-OH(e), C_4-OH(a)] forms a cyclic carbonate[68] (XLV). The sequence of chromatographic elution[68] and velocity of hydrolysis[68] of the diol diacetates are also in agreement with the configurations assigned.

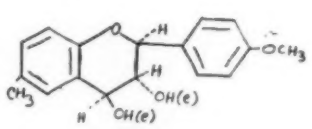


(XLII)
trans-6-Methyl-4′-methoxydihydroflavonol

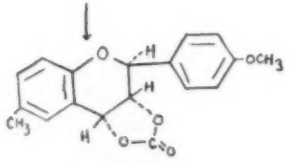
| $LiAlH_4$



(XLIII)
2,3-*trans*-3,4-*cis*-6-Methyl-4′-methoxy-flavan-3, 4-diol.



(XLIV)
2,3-*trans*-3,4-*trans*-6-Methyl-4′-methoxy-flavan-3, 4-diol.



(XLV)
Cyclic carbonate.

On the basis of these investigations, stereochemical configurations were assigned to synthetic leucoanthocyanidins, such, as allo- and isoallo-melacacidin tetramethyl ether[62], mollisacacidin trimethyl ether[70], guibourtacacidin dimethyl ether[71], allo-, and isoallo-teracacidin trimethyl ether[72], all of which have been proved to be true by independent stereochemical investigations from other laboratories[35,53,73].

Stereochemistry of 3-Bromoflavanones

Stereochemistry of 3-bromoflavanones and the corresponding bromohydrins needed to be first established so that the stereochemical pattern for the third racemate could be evolved. Limaye[74] reported the conversion of the isomer (m.p. 138°) into its epimer (m.p. 167°) by boiling it with acetic acid-hydrochloric acid. The latter could not be converted into the former[74]. These facts led us to propose that the stable isomer (m.p. 167°) possessed a favoured (2,3-*trans*) configuration and its epimer (m.p. 138°), 2,3-*cis*-configuration[68]. I.R. spectroscopic studies of ∝-halogeno-cyclic ketones have helped to assign conformation to halogen atoms[75]. A band of lower frequency (663 cm^{-1}) in the infrared curve of the lower melting isomer indicated C_3-Br axial and a band of higher frequency (752 cm^{-1}) in the curve of its isomer[68] showed it to be equatorial[76]. This physical evidence is in agreement with the configurations suggested earlier[68] for the isomeric 3-bromoflavanones. These were finally confirmed by the chemical evidence, *i.e.*, studying velocity of dehydrobromination[77] of both the isomers. On the basis of a, a-*trans* elimination principle, the isomer with C_2-H(a), C_3-Br(a) would be dehydrobrominated faster than the one with C_2-H(a), C_3-Br(e). The velocity of dehydrobromination of both the isomers measured U.V. spectroscopically noting the intensity of absorption at the maximum 3200Å of the

flavone formed, indeed proved that it was so. Thus, this novel kinetic approach confirmed the assignments, *i.e.*, the lower melting isomer (XLVI) has 2,3-*cis*-configuration [C_2-Ph(e), C_3-Br(a)], whereas the higher melting isomer (XLVII) has 2,3-*trans*-configuration [C_2-Ph(e), C_3-Br(e)].

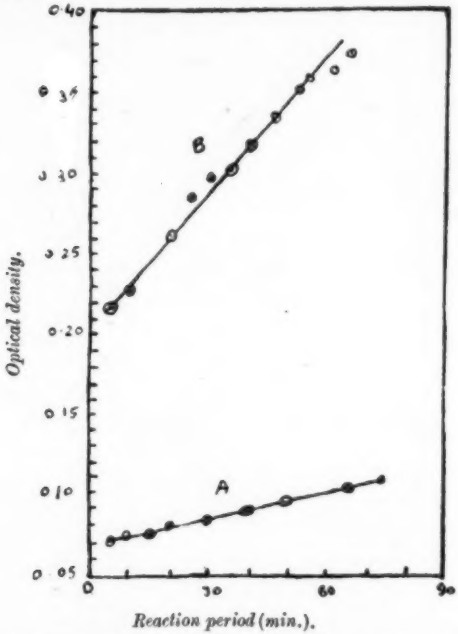


FIG. 1. Dehydrobromination of (A) 6-methyl-4′-methyoxy-3-bromoflavanone (m.p. 167°) and (B) 6-methyl 4′-methoxy-3-bromoflavanone (m.p. 138°).

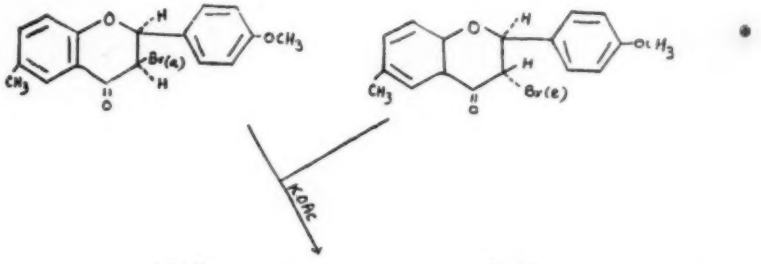
Stereochemistry of the Bromohydrins

C_4-OH of the isomeric bromohydrins can be either equatorial or axial. Its conformation in both of them was settled[77] by reductively debrominating them with lithium aluminium hydride and isolating the identical flavan-4-ol (LIV), which was previously synthesised by hydrogenating the flavanone over platinum catalyst in an acidic medium. Thus the bromohydrin (XLIX) (m.p. 200°) was assigned 2,3-*cis*-3,4-*trans*-configuration [(C_2-PH(e), C_3-Br(a), C_4-OH(a)] and the other bromohydrin (L) (m.p. 175°) was assigned 2,3-*trans*-3,4-*cis*-configuration[77] [C_2-Ph(e), C_3-Br(e), C_4-OH(a)]. Here it may be pointed out that the use of lithium aluminium hydride, which is sometimes known to debrominate through an epoxide formation[78], does not introduce any doubt in the above stereochemical conclusion since such a mechanism could only affect the C_3-Br bond and not the C_4-OH bond.

Stereochemistry of the Third Racemate

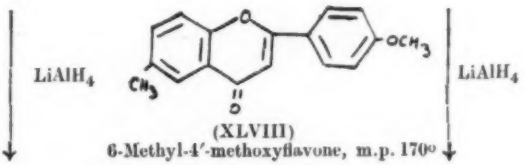
The diacetate (LIII) of 6-methyl-4′-methoxyflavan-3,4-diol, synthesised from the bromohydrin, with 2,3-*cis*-3,4-*trans*-configuration [C_2-Ph(e), C_3-Br(a), C_2-OH(a)] by treatment with potassium acetate in alcohol is different from the diacetates of the first two racemates, which are isomeric in position '4'. It follows by exclusion that this racemate must have a different configuration, *i.e.*, C_3-$OCOCH_3$ must be axial. Taking into consideration the

axial conformation of C_4-OH of the bromohydrin, it was therefore assigned 2,3-*cis*-3,4-*trans*-configuration[68] [C_2-Ph(e), C_3-$OCOCH_3$(a), C_4-$OCOCH_3$(a)]. Further, on treatment with sodium hydroxide in dioxane, the 3-bromoflavan-4-ol (XLIX) gave an epoxide[68] (LI), which on opening with acetic acid – sulphuric acid and acetylation gave the same diol diacetate (LIII). This may be explained on the basis of the accepted mechanism of the formation of an epoxide with inversion at the C_3-Br bond[79], *i.e.*, C_3-Br(a) $\longrightarrow$ C_3-O(e) and its *trans*-a, a-opening[80,83]. Thus the diol diacetate should have both C_3-$OCOCH_3$ and C_4-$OCOCH_3$ axial. Inversion at C_3-Br, *i.e.*, C_3-Br(a) $\longrightarrow$ C_3O(e), assumed to take place during the formation of the epoxide, does not militate the explanation given above for the retention of configuration as it is well established by Weinstein[84] and Shoppee[85] that the solvent and the reagent play a very important part in deciding the halogen replacement mechanism.

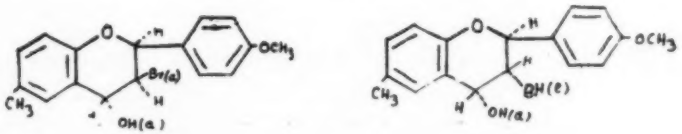


(XLVI)
cis-6-Methyl-4′-methoxy-3-bromoflavanone.

(XLVII)
trans-6-Methyl-4′-methoxy-3-bromoflavanone.



(XLVIII)
6-Methyl-4′-methoxyflavone, m.p. 170°



(XLIX)
2,3-*cis*-3,4-*trans*-6-Methyl-4′-methoxy-3-bromoflavan-4-ol.

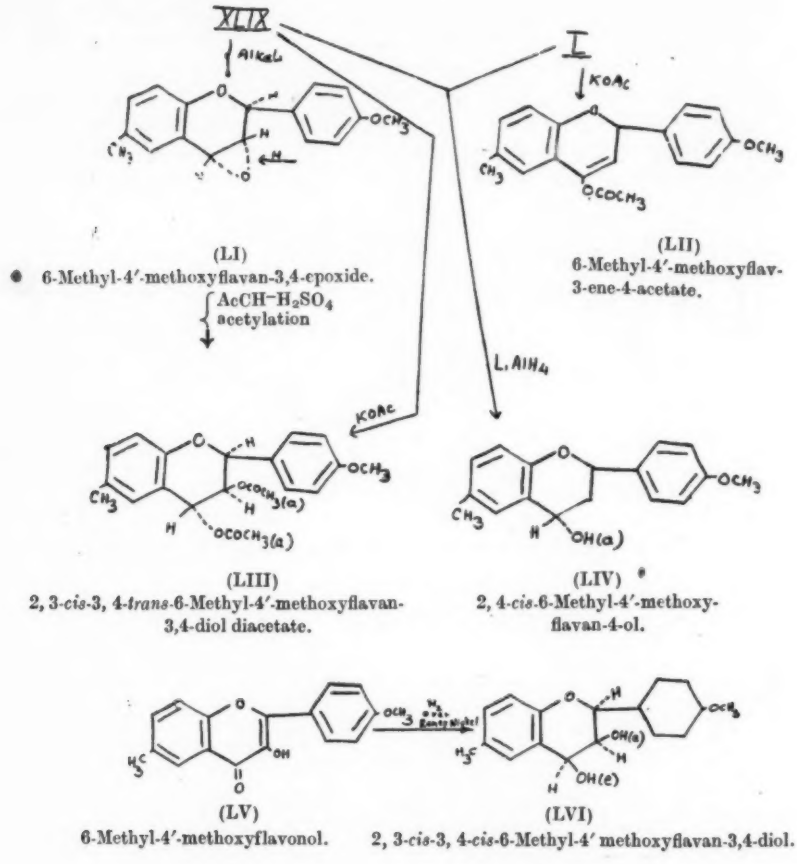
(L)
2,3-*trans*-3,4-*cis*-6-Methyl-4′-methoxy-3-bromoflavan-4-ol.

Stereochemistry of the Fourth Racemate

The remaining fourth racemate (LVI) would have 2,3-*cis*-3,4-*cis*-configuration [C_2-Ph(e), C_3-OH(a), C_4-OH(e)], the same as assigned to the synthetic melacacidin derivative by King and Clark-Lewis[53]. This assignment of these authors is complementary to our above assignments to the three racemates and is in agreement with both the formation of cyclic carbonate from their diol and the generalisation of catalytic *cis*-addition of hydrogen to the double bond of the flavonol and formation of the comparatively stable isomer.

Thus these complicated synthetic and stereochemical investigations extending over six

years were brought to a successful conclusion and a substantial contribution to the stereochemistry of flavans, which was so little known in 1954 (with the exception of catechins) when these investigations were undertaken, was made.



Synthesis of Naturally Occurring Dihydroflavonols

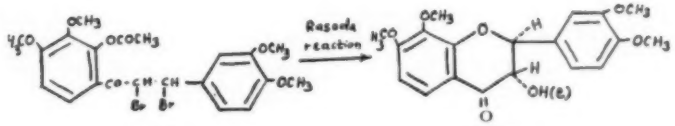
In connection with the work on flavan-3, 4-diols, the method of Limaye[86] for the synthesis of dihydroflavonols was well standardised. This was extended and the naturally occurring dihydroflavonols—fustin and dihydrorobinetin—were synthesised[87] as their trimethyl ether and tetramethyl ether, respectively. The chalkone acetate was converted through its dibromide to the corresponding dihydroflavonol (LXXIV) by boiling with aqueous acetone-sodium carbonate and thus fustin trimethyl ether was obtained. Similarly 2′-acetoxy-4′, 2, 4, 5-tetramethoxychalkone was brominated and the dibromide was cyclised with aqueous acetone-sodium carbonate to dihydrorobinetin tetramethyl ether (LXIX). The synthetic sample showed no depression in a mixed melting point determination with the tetramethyl ether of the natural dihydrorobinetin, kindly supplied by Prof. Freudenberg[88].

Synthesis of Naturally Occurring Leucoanthocyanidins or their Epimers

Once the methods for the synthesis of leucoanthocyanidins were evolved, we directed our attention to the syntheses of naturally occurring ones.

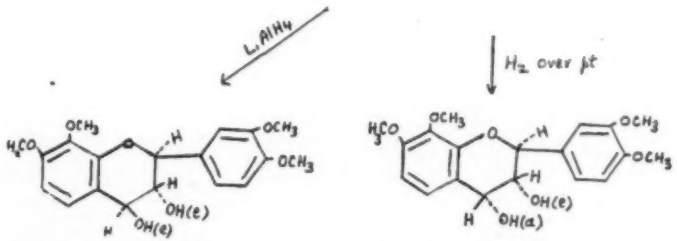
Melacacidin.—King and co-workers[56] isolated the first leuccanthocyanidin, melacacidin, as its tetramethyl ether in a crystalline form. The following sequence of reactions to achieve its synthesis gave us its epimers[58-62].

2′-Acetoxy-3′,4′,3,4-tetramethoxychalkone was converted through its dibromide (LVII) to the corresponding dihydroflavonol (LVIII). The latter was reduced with lithium aluminium hydride to a colorless flavan-3,4-diol (LIX). When the dihydroflavonol (LVIII) was hydrogenated over platinum catalyst in acetic acid, the other racemate (LX) was obtained. From models and geometrical considerations, the first racemate (LIX) was assigned 2,3-*trans*-3,4-*trans*-configuration [C_2-Ph(e), C_3-OH(e), C_4-OH(e)] and the second one (LX) 2,3-*trans*-3,4-*cis*-configuration[55] [C_2-Ph(e), C_3-OH(e), C_4-OH(a)]. Later investigators[53], as discussed above, confirmed these stereochemical assignments. The racemates can now be designated as alloiso- and allo-melacacidin derivatives, respectively.



(LVII)
2′-Acetoxy-3′, 4′-3, 4-tetramethoxychalkone dibromide.

(LVIII)
trans-7,8,3′,4′-Tetramethoxydihydroflavonol.

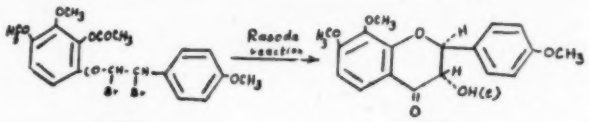


(LIX)
2, 3-*trans*-3,4-*trans*-7,8,3′,4′-Tetramethoxyflavan-3,4-diol (alloisomelacacidin tetramethyl ether).

(LX)
2, 3-*trans*-3,4-*cis*-7,8,3′,4′-Tetramethoxyflavan-3,4′-diol (allomelacacidin tetramethyl ether).

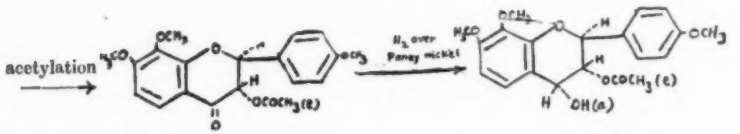
Teracacidin.—Clark-Lewis and Mortimer[35] recently reported the isolation of new leucoanthocyanidins, teracacidin and isoteracacidin, from *Acacia intertexta*. They have further shown that teracacidin has 7,8,4′-trihydroxyflavan-3,4-diol structure and is stereochemically analogous to melacacidin, *i.e.*, it has 2,3-*cis*-3,4-*cis*-configuration [C_2-Ph(e), C_3-OH(a), C_4-OH(e)] and isoteracacidin is its epimer and has 2,3-*cis*-3,4-*trans*-configuration [C_2-Ph(e), C_3-OH(a), C_4-OH(a)]. 7,8,4′-Trimethoxydihydroflavonol (LXII) was prepared by cyclisation of the corresponding acetoxychalkone dibromide (LXI) by the Rascda reaction[86] and its acetate (LXIII) was reduced with hydrogen over Raney nickel when the corresponding leucoanthocyanidin monoacetate (LXIV) was obtained. On hydrolysis, the flavan-3,4-diol (LXV) could be isolated[72]. The dihydroflavonol (LXVI) on reduction with lithium aluminium hydride gave a mixture of isomeric flavan-3,4-diols, which was difficult

to separate. On several crystallisations the other racemate (LXVIII) could be isolated[72]. The flavan-3, 4-diols (LXVII) and (LXVIII) have been assigned 2,3-*trans*-3,4-*cis*- [C_2-Ph(e), C_3-OH(e), C_4-OH(a)] and 2,3-*trans*-3,4-*trans*-configurations [C_2-Ph(e), C_3OH(e), C_4-OH(e)] and have been called as allo- and alloiso-teracacidin, respectively.



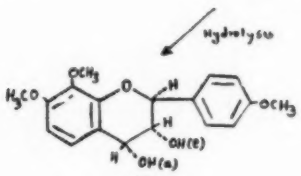
(LXI) (LXII)

2′-Acetoxy-3′,4′,4-trimethoxychalkone dibromide. *trans*-7,8,4′-Trimethoxydihydroflavonol.



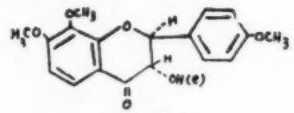
(LXIII) (LXIV)

trans-7,8,4′-Trimethoxydihydroflavonol acetate. 2, 3-*trans*-3, 4-*cis*-7,8,4′-Trimethoxy-3-acetoxyflavan-4-ol.



(LXV)

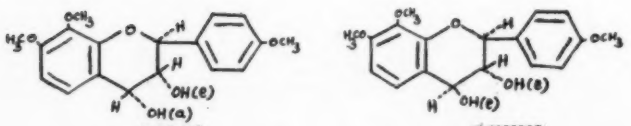
2, 3-*trans*-3, 4-*cis*-7,8,4′-Trimethoxyflavan-3,4-diol (alloteracacidin trimethyl ether).



(LXVI)

trans-7,8,4′-Trimethoxydihydroflavonol

$LiAlH_4$

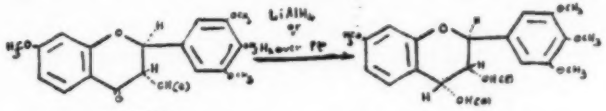


(LXVII) (LXVIII)

2, 3-*trans*-3, 4-*cis*-7,8,4′-Trimethoxyflavan-3,4-diol (alloteracacidin trimethyl ether). 2,3-*trans*-3,4′-*trans*-7,8,4′-Trimethoxyflavan-3,4-diol (alloisoteracacidin trimethyl ether).

Leucorobinetinidin.—Synthesis of the naturally occurring dihydroflavonol, dihydrorobinetin, as its tetramethyl ether (LXIX) has already been described above. It was reduced with lithium aluminium hydride, when a mixture of two compounds was obtained. On several crystallisations the pure leucoanthocyanidin (LXX) could be isolated[89]. Its stereo-

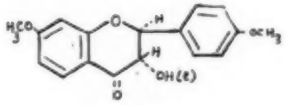
specific synthesis could be achieved by hydrogenating the dihydroflavonol over platinum black in acetic acid. From the method of synthesis, it follows that it has 2,3-*trans*-3,4-*cis*-configuration [C_2-Ph(e), C_3-OH(e), C_4-OH(a)] and in all probability belongs to the same stereochemical series as that of (−) -leucorobinetinidin, recently isolated by Weinges[30].



(LXIX) (LXX)

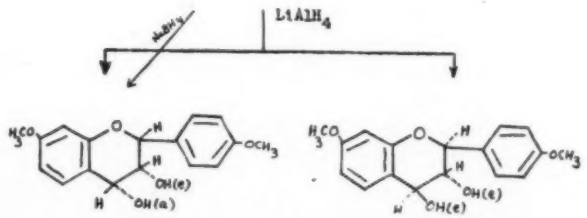
trans-7,3′,4′, 5′-Tetramethoxydihydroflavonol. 2,3-*trans*-3, 4-*cis*-7,3′,4′,5′-Tetramethoxyflavan-3, 4-diol(leucorobinetinidin tetramethyl ether)

Guibourtacacidin.—Roux[34] indicated the presence of a new leucoanthocyanidin, "Guibourtacacidin", in the species of genus *Guibourtia* and suggested it to be 7,4′-dihydroxyflavan-3, 4-diol. We extended our method for its synthesis as the dimethyl ether. 7,4′-Dimethoxydihydroflavonol (LXXI) was reduced with lithium aluminium hydride and the mixture of isomeric flavan-3,4-diols was conveniently separated by acetylating it and fractionally crystallising the diacetates. The diacetate of diol (LXXII) separated at first. On hydrolysis the corresponding diol (LXXII) could be obtained[71]. The mother liquor of crystallisation of the acetates was then hydrolysed and the second diol (LXXIII) was isolated[71]. The first (LXXII) of these isomeric diols could be obtained in a quantitative yield on reduction of the dihydroflavonol (LXXI) with sodium borohydride. On the basis of stereospecificity of reducing agents and our hypothesis regarding the stereochemical configurations of flavan-3, 4-diols, the diol (LXXII) was assigned 2,3-*trans*-3,4-*cis*-configuration [C_2-Ph(e), C_3-OH(e), C_4-OH(a)] and is almost certainly identical with the dimethyl ether of the natural guibourtacacidin[71]. The other diol (LXXIII) would then have 2,3-*trans*-3,4-*trans*-configuration [C_2-Ph(e), C_3-OH(e), C_4-OH(e)].



(LXXI)

trans-7,4′-Dimethoxydihydroflavonol.



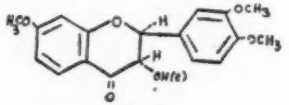
(LXXII) (LXXIII)

2,3-*trans*-2, 4-*cis*-7,4′-Dimethoxyflavan-3:4-diol (guibourtacacidin dimethyl ether) 2,3-*trans*-3,4-*trans*-7,4′-Dimethoxyflavan-3,4-diol.

Mollisacacidin.—Keppler[26] isolated (±)-mollisacacidin from *Acacia mollissima* and assigned to it 7,3′,4′-trihydroxyflavan-3,4-diol structure. Its identity with gleditsin, isolated from *Gleditsia japonica* (Miquel) by Mitsuno and Yushizaki[90], was established by Clark-Lewis and Mitsuno[91]. Recently (−)-leucofisetinidin was isolated from quebracho wood by

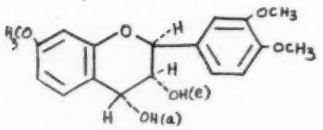
Freudenberg and co-workers[27-29] and was shown to be enantiomorphous with (±)-mollisacacidin. The latter was partially synthesised by Keppler[26] by hydrogenation of fustin, obtained from *Rhus glabra*. Simultaneously, Chandorkar and Kulkarni[70] prepared (±)-fustin trimethyl ether (LXXIV), reduced it with lithium aluminium hydride, isolated two isomers (LXXV and LXXVI) of 7,3′,4′-trimethoxyflavan-3, 4-diol, and assigned to one of them (LXXV) a 2,3-*trans*,-3,4-*cis*-configuration [C_2-Ph(e), C_3-OH(e), C_4-OH(a)] and suggested its possible identity with the corresponding (±)-mollisacacidin derivative. Clark-Lewis and Roux[73] confirmed this suggestion by a mixed melting point determination and infrared measurements on the diacetates.

The above leucoanthocyanidins were synthesised as their methyl ethers, whereas in nature they occur as phenols. Synthesis of leucoanthocyanidins with free phenolic hydroxy groups was therefore undertaken. So far synthetic crystalline leucoanthocyanidins have been obtained by hydrogenation of the naturally occurring dihydroflavonols[26,29,51,52,92] Synthesis of (±)–mollisacacidin (LXXX), reported by us[93], therefore forms the first total synthesis of a crystalline (±) leucoanthocyanidin with free phenolic hydroxy groups. 2′-Acetoxy-4′, 3, 4-tribenzyloxychalkone dibromide (LXXVII) was cyclised to the corresponding dihydroflavonol (LXXVIII). It was reduced with sodium borohydride when the *cis*-diol was obtained in a quantitative yield. 7,3′,4′-Tribenzyloxyflavan-3, 4-diol (LXXIX), thus obtained, was smoothly converted into (±)-mollisacacidin (LXXX) by dissolving it in dimethyl formamide and debenzylating it by hydrogen over Pd/C. It was crystallised from luke warm water. This diol would have 2,3-*trans*-3,4-*cis*-configuration [C_2-Ph(e), C_3-OH(e), C_4-OH(a)] and hence belong to the same stereochemical series as the naturally occurring mollisacacidin. The identity of this synthetic (±)–mollisacacidin with the racemate prepared from the naturally occuring enantiomorphs of mollisacacidin was estabiished by Clark-Lewis (private communication) by mixed melting point and infrared determinations. We are grateful to him for the same.

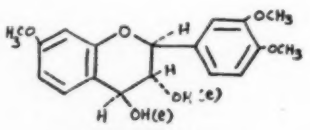


(LXXIV)
trans-7,3′4′-Trimethoxydihydroflavonol

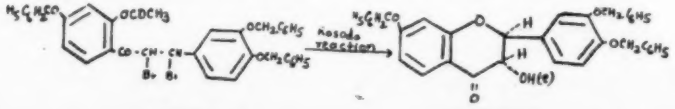
$LiAlH_4$



(LXXV)
2,3-*trans*-3,4-*cis*-7,3′,4′-Trimethoxyflavan-3,4-diol (mollisacacidin trimethyl ether).



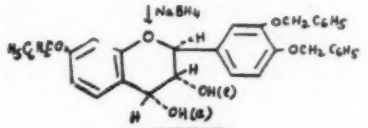
(LXXVI)
2,3-*trans*-3-4-*trans*-7,3′,4′-Trimethoxy-finvan-3,4-diol.



(LXXVII)
2′-Acetoxy-4′3,4-tribenzyloxychalkone dibromide.

(LXXVIII)
trans-7,3′,4′-Trinenzyloxydihydro-flavonol.

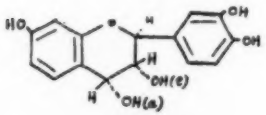
(LXXVIII)



(LXXIX)

2,3-*trans*-3,4-*cis*-7,3′,4′-Tribenzyloxyflavan-3,4-diol.

H_2 over Pd/C



(LXXX)

2,3-*trans*-3,4-*cis*-7,3′,4′-Trihydroxyflavan-3,4-diol [(±)-mollisacacidin].

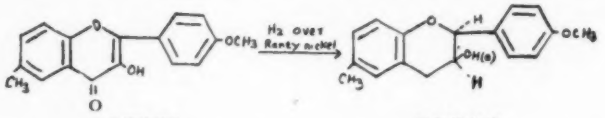
A New Method for the Synthesis of Catechins

Lastly I would like to deal with an interesting offshoot of the above investigations, *i.e.*, a novel method evolved in our laboratory for the synthesis of isomeric catechins. 3-Hydroxyflavans or catechins have been extensively studied for the last thirty years by Freudenberg and his school. 3,5,7,3′,4′-Pentahydroxyflavan was isolated in all the possible four optically active and two racemic forms[94]. It is now conclusively proved that (+)-catechin is the *trans*-isomer and (−)-epicatechin, the *cis*-one [95-97]. Birch and co-workers[98] used the elegant atrolactic acid method of Prelog and co-workers[99] and assigned absolute configurations to (+)-catechin and (−)-epicatechin.

Synthetic catechins are generally prepared by hydrogenation of flavonols[100] or flavylium salts[95,101]. Only one racemate belonging to the epicatechin series is obtained in each case though theoretically two can exist. (+)-Catechin could be epimerised to (+)-epicatechin[94] and (−)-epicatechin to (−)-catechin[94]. A method for the direct synthesis of a racemate belonging to the catechin series was, however, until recently unknown. Freudenberg and co-workers[29-30] obtained *trans*-catechins by hydrogenolysis of the naturally occurring dihydroflavonols. The latter method is obviously of a limited applicability.

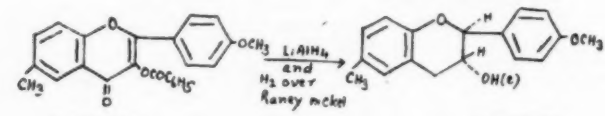
Kashikar and Kulkarni[36] reported for the first time the synthesis of both the possible racemates of 6-methyl-4′-methoxy-3-hydroxyflavan. One of the racemates (LXXXII) belonging to the epicatechin series was obtained by hydrogenation of the corresponding flavonol (LXXXI), whereas the other racemate (LXXXIV) was synthesised by reduction of the flavonol benzoate (LXXXIII) with lithium aluminium hydride and subsequent hydrogenation of the complex *in situ* over Raney nickel. It was later on found that instead of the flavonol benzoate (LXXXIII), if the benzyl ether (LXXXV) was used for the reduction, the yield of the isomer could be improved[102]. In this procedure a two-stage reduction of the flavonol benzylether is involved. Theoretically, such a reduction may lead to the formation of either a 4-hydroxyflavan or a 3-hydroxyflavan. That the new diastereoisomer is a 3-hydroxyflavan has been proved by the isolation of an intermediate, 7, 3′,4′-trimethoxy-3-benzyloxy flavan (LXXXVIII), from the corresponding flavonol benzyl ether (LXXXVII) in the synthesis of (+)-fisetinidol trimethyl ether (LXXXVI) and its conversion to the same catechin[103]. On treatment with phosphorus pentachloride, 6-methyl-4′-methoxy-3-hydroxyflavan (LXXXIV), prepared by this method, gave the corresponding 2-chloroisoflavan[102] (LXXXVI), characteristic of a *trans*-catechin[103]. This stereochemical

assignment was further confirmed by a lowering in mixed melting point of (±)-afzelechin trimethyl ether [(±)-*trans*-5,7,4′-trimethoxy-3-hydroxyflavan[102]] (XCI), synthesised by the above method with (−)-epiafzelechin trimethyl ether [(−)-*cis*-5,7,4′-trimethoxy-3-hydroxyflavan], kindly sent by Prof. King[95]. The above stereochemical assignments to the catechins are tentative and their confirmation by I. R. data is awaited.



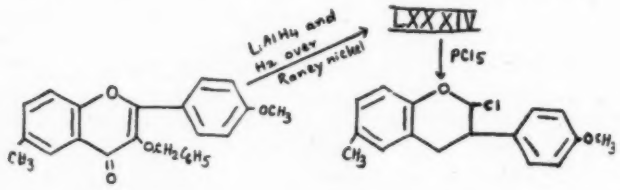
(LXXXI)
6-Methyl-4′-methoxyflavonol.

(LXXXII)
cis-6-Methyl-4′-methoxy-3-hydroxyflavan.



(LXXXIII)
6-Methyl-4′-methoxyflavonol benzoate.

(LXXXIV)
trans-6-Methyl-4′-methoxy-3-hydroxyflavan.

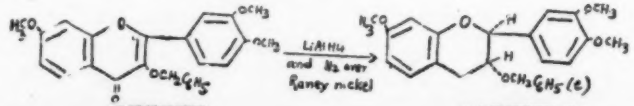


(LXXXV)
6-Methyl-4′-methoxyflavonol benzyl ether.

(LXXXVI)
6-Methyl-4′-methoxy-2-chloroiso-flavan.

Synthesis of (±)-*Fisetinidol Trimethyl Ether,* (±)-*Robinetinidol Tetramethyl Ether and* (±)-*Afzelechin Trimethyl Ether*

This new method was then extended to the synthesis of the naturally occurring catechins. 7,3′,4′-Trimethoxyflavonol benzyl ether (LXXXVII) was reduced with lithium aluminium hydride, the complex *in situ* was hydrogenated over Raney nickel, and the corresponding 3-benzyloxyflavan (LXXXVIII) was isolated. It was further debenzylated with hydrogen over Raney nickel to (±)-fisetinidol trimethyl ether[102] (LXXXIX). Similarly 7,3′,4′,5′-Tetramethoxyflavonol benzyl ether (XC) under the above experimental conditions gave the corresponding 3-hydroxyflavan (XCI), *i.e.* (±)-robinetinidol tetramethyl ether. A considerable time was spent in preparing 5,7,4′-trimethoxyflavonol benzyl ether (XCII) through the corresponding flavanone, 3-nitroscflavanone, and flavanol. The benzyl ether (XCII) on reduction gave the catechin (XCIII) which could be first isolated in a crystalline form as its acetate. On hydrolysing the latter, (±)-afzelechin trimethyl ether[102] (XCIII) could be synthesised.

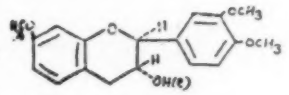


(LXXXVII)
7,3′,4′,-Trimethoxyflavonol benzyl ether.

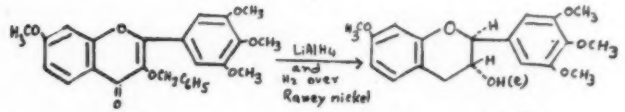
*(LXXXVIII)
trans-7,3′,4′-Tirmethoxy-3-benzyloxyflavan.

* H and OCH_2Ph (e) linkings will be on simple lines and not in dotted lines as shown.

(LXXXVIII) —H_2 over Raney nickel→

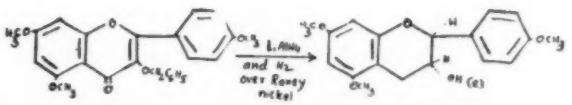


*(LXXXIX)
trans-7,3′,4′-Trimethoxy-3-hydroxyflavan
[(±)fisetinidol trimethyl ether].



(XC)
7,3′,4′,5′-Tetramethoxyflavonol benzyl ether.

*(XCI)
7,3′,4′,5′-Tetramethoxy-3-hydroxflavan
[(±)-robinetinidol tetramethyl ether].



(XCII)
5,7,4′ Trimethoxyflavonol benzyl ether.

*(XCIII)
5-7,4′-Trimethoxy-3-hydroxy flavan
[(±) afzechin trimethyl ether].

In conclusion, it may be stated that the above work represents the first systematic investigations on the synthesis and stereochemistry for leucoanthocyanidins and the related compounds. The primary object of the synthesis of all the four racemates of a leucoanthocyanidin was realised. For the first time, Barton's concept of conformational analysis was introduced in this field and the stereochemistry of leucoanthocyanidins and related compounds was placed on a firm footing. Incidentally, both the synthetic and the natural dihydroflavonols were assigned stereochemical configurations, which have been confirmed later by several investigators. With the judicious use of metal hydrides and other hydrogenating catalysts, several naturally occurring compounds, such as, fustin trimethyl ether, dihydrorobinetin tetramethyl ether, guibourtacacidin dimethyl ether, leucorobinetinidin tetramethyl ether, and mollisacacidin were synthesised. A new method was developed for the synthesis of catechins and synthesis of (±)—fisetinidol trimethyl ether, (±)—robinetinidol teramethyl ether and (±)—afzelechin trimethyl ether was accomplished.

The above work was carried out in collaboration with my colleagues, Dr. C. G. Joshi, Dr. V. R. Shah at the National Chemical Laboratories, Poona, and Shri M. D. Kashikar, Dr. D. M. Phatak, Dr. K. R. Chandorkar, Dr. N. B. Mulchandani, Shri R. S. Kulkarni, and Kum. A. M. Borkar at the Institute of Science, Bombay. I take this opportunity to express my sincere thanks to them for participating in this team-work.

* H and (e) linkings will be in simple lines and not in dotted lines as shown.

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[Jour. Indian Chem. Soc., Vol. 38, No. 5, 1961]

Studies in Zirconium Oxide Sols. Part I. Electrical Conductance of Zirconium Oxide Sols

A. M. Trivedi, I. M. Bhatt, and M. J. Patani

Concentrated zirconium oxide sols of fairly high degree of purity have been prepared by hydrolysing zirconium nitrate, followed by continued hot dialysis. When diluted sols are allowed to age, the specific conductance increases due to desorption of the adsorbed electrolyte. In the case of the concentrated sol, ageing results in the decrease of specific conductance due to aggregation of the particles. Equivalent conductance of the micelles on dilution first decreases and then increases on further dilution, showing the behaviour of a typical colloidal electrolyte.

Trivedi, Divatia, and Patani (*Proc. Ind. Aead. Sci.*, 1952, **36A,** 530 et seq.) pointed out that the equivalent conductance of the micelles in a colloidal system decreased on dilution and then increased on further dilution, the latter being the normal behaviour of an electrolyte. In the present investigation, conductance of zirconium oxide sol has been studied and it has been concluded that the curve of equivalent conductance against the square root of concentration passes through a minimum; this behaviour is more marked when the purity of the sol is increased. Zirconium oxide sol was previously studied by Sharma and Dhar (this *Journal*, 1932, **9**, 455), who observed an increase in conductance on ageing. This has been confirmed in the present investigation.

EXPERIMENTAL

Several methods may be employed to prepare zirconium oxide sols (Blitz, *Ber.*, 1902, **35,** 4431; Ruer, *Z. anorg. Chem.*, 1905, **43,** 282; Sharma and Dhar, *loc. cit.*). In the present investigation, the sol was prepared by hydrolysis of zirconium nitrate, following the method of Sharma and Dhar (*loc. cit.*). The sol so obtained was subjected to continued hot dialysis (Neidle and Barab, *J. Amer. Chem. Soc.*, 1916, **38**, 1962; 1917, **39,** 71.). In this way a fairly concentrated sol was obtained, which remained stable for at least one year.

Zirconium oxide content was determined by drying the sol (5c.c.) at 110-20° and finally igniting it on a burner. The nitrate content was determined by the procedure suggested by Kolthoff (*J. Amer. Chem. Soc.*, 1933, **55,** 1454). The sol (5c.c.) was coagulated with sodium sulphate and washed till free of nitrate, as tested by brucine (B. D. H., "Organic Reagents for Analytical Uses", 1949, p. 29). To the filtrate and washings an excess of a standard solution of ferrous sulphate was added. The unconsumed ferrous sulphate was backtitrated against a standard solution of potassium dichromate, using diphenylamine as an indicator. Free zirconium was found to be absent. Purity of the sol is expressed as the ratio of ZrO_2 to NO_3^-, both being expressed in terms of g./litre. The relevant data are recorded in Table I.

TABLE I

Sol.	ZrO_2. (*a*)	Conc. of NO_3^-. (*b*)	Purity. (*a*/*b*)
G	30.5 g./litre	3.142 g./litre	10
H	25.6	2.067	12
I	21.6	1.034	21
L	22.2	1.736	13

Change in Conductance on Ageing.—The conductance of zirconium oxide sol was determined over a number of days. Doubly distilled water (sp. cond. $=2.0\times10^{-6}$ mhos at 35°) was employed for dilution, its conductance being neglected. The dilutions were checked by analysis. The conductance of the sol was measured at 35°. Three sols were examined. Their behaviour being found similar, some of the results of one of them (sol L) are recorded in Table II.

TABLE II

Sol L.

No. of days.	Specific conductance $\times 10^4$			
	100%.	50%.	25%.	12.5%.
0	11.740	5.824	3.249	2.369
7	11.700	5.848	3.331	2.452
26	11.610	5.882	3.487	2.500
63	11.600	6.057	3.909	2.870
104	11.600	6.172	4.107	2.929

Change in Conductance on Dilution.—Three sols (G, H, and I) were diluted to different extents and changes in conductance on dilution were measured. The data regarding the specific and equivalent conductances in the case of sol I are recorded in Table III.

TABLE III

Sol I.

Conc. of ZrO_2 sol.	Conc. of NO_3^- in the micelles.	Conductance of the micelles. specific.	Equiv. (λ)	Change in equiv. conduct. (λ).
21.60 g./litre	50.00 m.e./litre	9.649×10^{-4}	19.300	111.8%
19.44	45.00	8.638	19.200	111.2
17.28	40.00	7.561	18.900	109.4
15.12	35.00	6.407	18.310	106.0
12.96	30.00	5.370	17.900	103.6
10.80	25.00	4.316	17.270	100.0
8.64	20.00	3.469	17.350	100.5
6.48	15.00	2.660	17.730	102.7
4.32	10.00	1.928	19.280	111.6
2.16	5.00	1.379	27.390	158.6

DISCUSSION

Effect of Ageing.—It is observed that the specific conductance increases on ageing, the behaviour being more marked, the greater the dilution. On the other hand, in the case of original sol there is a tendency towards a decrease in specific conductance on ageing. Similar behaviour was noticed before (Jha and Ghosh, this *Journal*, 1945, **22**, 271; Parikh *et al.*, *ibid.*, 1959, **38**, 711). Ageing brings into play two opposing tendencies: (*a*) aggregation of micelles leading to the decrease in specific conductance and (*b*) desorption of the stabilising electrolyte which leads to the increase in specific conductance. The former tendency is prominent in the case of concentrated sols, whereas the latter comes into prominence as the sols are diluted.

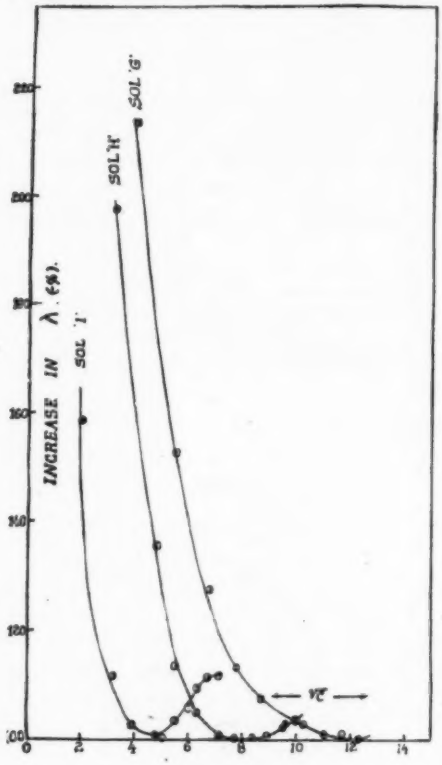

FIG. 1

Effect of Dilution.—Sols G, H, and I, which were of the order of increasing purity, were examined for the effect of dilution. In the first place, in all cases the specific conductance of the sol decreases on increasing the purity (data not given). Again, as noted previously, the conductance decreases on dilution and then increases, the effect becoming more marked as the purity is increased. To obtain the relation between conductance and dilution in the case of sols of different degrees of purity, the lowest value of the equivalent conductance in each case has been taken as 100% and the corresponding increase or decrease is plotted against the square root of the concentration (see Fig. 1). The detailed data of sol I are given in Table III. Hence zirconium oxide sols may also be classified as a colloidal electrolyte (Parikh *et al.*, *loc. cit.*).

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Studies in Zirconium Oxide Sols. Part II. Hydration of Micelles in Zirconium Oxide Sols

A. M. Trivedi, I. M. Bhatt, and M. J. Patani

Hydration of the micelles in the case of zirconium oxide sol has been studied by considering the distribution of an electrolyte (NH_4Cl) as a reference substance across a semipermeable membrane. Neglecting the membrane equilibrium effect, the value of hydration comes out to be 62 moles of water per mole of zirconium oxide. This value is in agreement with that obtained by viscosity method. The charge on the micelles has been found to be 0.4 m.e. of NO_3^- per g. of zirconium oxide.

Properties of metallic oxide sols are known to be governed by the charge as well as the solvation of the micelles. Coagulation of a sol by a mixture of electrolytes may partly be explained by the change in hydration of the micelles in presence of foreign substances. Very few attempts have been made to measure the extent of hydration quantitatively. In the present investigation, hydration of micelles has been measured by studying the distribution of ammonium chloride across a semipermeable membrane in presence of colloidal zirconium oxide. Alternatively, viscosity measurements may also be employed to measure the extent of hydration.

EXPERIMENTAL

Methods of preparation and analysis of zirconium oxide sols have been reported earlier (this *issue*, p. 288). To determine NH_4^+ ion, an aliquot portion of the sol was coagulated with sodium sulphate, filtered, and washed till free of ammonium ion. An excess of a standard solution of NaOH was added to the filtrate and washings. The solution was then boiled till free of ammonia, cooled, an excess of a standard HCl solution added, and the unused acid was titrated against NaOH (Vogel, "A Text-Book of Quantitative Inorganic Analysis", 1955, p. 505).

A partially dialysed sol was mixed with ammonium chloride (far below its c.v.) and was kept in collodion bags, suspended in water. After equilibrium, the sol inside and the liquid outside the bag were analysed. ZrO_2 was found to be absent outside the bag. Some of the results are shown in Table I.

TABLE I

ZrO_2 conc. (I—E)*.	Diff. in NO_3^- (I—E).	Conc. of NO_3^- (m. e. per g. of colloid) $\frac{NO_3^-\ (I-E)}{ZrO_2\ (I-E)}$.	Conc. of ammonium ion (m.e./litre). I.	E.	D.	S.H.V.
23.20 g./litre	8.0 m.e./litre	0.34	8.88	11.28	0.1090	52.6
22.60	8.0	0.35	9.20	11.60	0.1092	52.5
22.60	8.0	0.35	8.96	11.36	0.1070	53.6
22.40	12.0	0.54	9.20	11.60	0.1083	52.9
23.20	12.0	0.52	9.12	11.68	0.1067	53.7
22.60	8.0	0.35	9.20	11.60	0.1092	52.5
	Mean	0.41			0.1082	52.9

*Concentration of ZrO_2 outside the membrane (E) is nil.

DISCUSSION

The concentration of ammonium ion outside the membrane appears from Table I to be greater than that inside the bag, reverse being the case with NO_3^- ions. The NO_3^- ions

are gegenions and are found both in the fixed and the free conditions. From the concentrations of NO_3^- ions inside and outsdide the bag, fixed NO_3^- ion/g. of zirconium oxide may be calculated; it comes out to be 0.4 m.e. of nitrate ion per g. of ZrO_2.

The unequal distribution of NH_4^+ ion across a semipermeable membrane may be due to (*a*) hydration of the micelles or (*b*) the membrane equilibrium effect. Either may be calculated if one is known. It was not found possible to measure either of these effects independently. If the concentration of the diffusible ion is much greater than that of the non-diffusible ion (only a fraction of which will be active towards membrane equilibrium), the membrane equilibrium effect may, however, be considered of lesser importance and the unequal distribution of NH_4^+ ion across the membrane may be attributed to the hydration effect. In that case, the apparent density (*D*) and specific hydrodynamic volume (S.H.V.) may be calculated as shown before (Trivedi and Patani, *Proc. Ind. Acad. Sci.*, 1954, **40A**, 119). Taking the average value of S.H.V. as 53 (Table I) and the density of zirconium oxide as 5.73 g./c.c. ("Chemical Engineer's Hand Book," 1941, p. 367), there will be 52 g. of non-solvent water to 5.73 g. of zirconium oxide. Thus, there are $(52/18)\times(1000/5.73)=504.1$ of m*M* water per g. of zirconium oxide. The molecular weight of zirconium oxide (ZrO_2) is 123.22. Therefore there are $(504.1/1000)\times 123.22=62$(approx.) moles of water per mole of zirconium oxide. The actual value of hydration will be slightly less than this value if the Donnan membrane equilibrium effect is taken in consideration.

Another method of evaluating the hydration of the micelles is to study the variation in specific viscosity of the sol on dilution. The method has been discussed in detail previously (Trivedi *et al.*, this *Journal*, 1957, **34**, 685). The hydration values, calculated in this way, were plotted against concentration. The apparent hydration values increase with increase in concentration so that the real value of hydration can be obtained by plotting the hydration values at lower concentrations and extrapolating the curve to zero concentration. The rapid increase in viscosity and apparent values of hydration are due to the non-Newtonian behaviour of the sol at a finite concentration. The values of hydration obtained by extrapolating the curve to zero concentration is found to be 55 moles of water per mole of zirconium oxide (data not given). Thus hydration values obtained by both the methods are of the same order. This was found also to be the case with aluminium oxide sols (Trivedi *et al., loc. cit.*).

To understand the contribution of hydration towards the stability of colloidal systems, it would be necessary to know not only the extent of hydration but also the nature of hydration. There are three types of bound water in colloidal systems (Jirgensons and Straumanis, "Colloidal Chemistry", 1954, p. 326):

(1) Tightly bound water (hydrogen bonds).
(2) Loosely adsorbed water by dipole attraction and cohesion.
(3) Immobilised water.

The last type exists principally in gels. The first type alone may have a definite value, whereas the second as well as the third will show wide variations. To determine the influence of hydration on stability, it will be necessary to determine the extent of each type of hydration. Only then it will be possible to comprehend the effect of solvation on the stability of colloidal systems.

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Studies on some Less Familiar Ferrocyanogen Complexes. Part IV*. Spectrophotometric and Conductometric Studies on Beryllium Ferrocyanide

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The reaction between potassium ferrocyanide and beryllium chloride has been studied spectrophotometrically. From the results it is concluded that (*i*) decomposition of K_4FeCy_6 is a slow reaction, (*ii*) the reaction is dependent on the concentration of beryllium ions, and (*iii*) it can best be studied at 450mμ.

Appearance of the blue colour in slightly acidic solution of potassium ferrocyanide in presence of beryllium ions has been explained on the basis of decomposition of potassium ferrocyande and the subsequent formation of Prussian blue. Conductometric titrations carried out at 30°, 60°, and 80° give evidence of the formation of an adsorption complex, $K_2BeFeCy_6.K_4FeCy_6$.

An interesting reaction, worth considering amongst the less familiar metal ferrocyanogen complexes, is the formation of beryllium ferrocyanide by the interaction of beryllium with potassium ferrocyanide. References on this compound are rarely met with in the literature. Recently the author came across a reference on the estimation of beryllium by ferrocyanide (Miss Zutshi, *Proc. Indian Sci. Cong.*, 1960, Part III, p. 191) where the reaction was assumed to be simple enough for indirect estimation of beryllium by titrating the excess of potassium ferrocyanide after precipitating beryllium as beryllium ferrocyanide. Our experience shows that the reaction is not so simple as that to be satisfactorily used for the estimation of beryllium in solutions. On the other hand, the reaction is enshrowded with a number of complexities, which should be taken into account while studying it.

Preliminary experiments reveal the following facts: (*i*) When dilute solutions of beryllium chloride and potassium ferrocyanide are mixed, a blue colour develops in a few moments; a turbidity appears on keeping it for four to five hours. (*ii*) On increasing the *p*H of the beryllium solution (just before precipitation of the oxide sets in; *p*H =4.5) a blue colour develops although it takes a little more time to do so. (*iii*) Dilute solutions, when mixed at a temperature near about 70°, give a white precipitate almost instantaneously although invariably tarnished with a green colour (turning to blue on keeping for more than 20 minutes at this temperature). (*iv*) On adding a concentrated solution of beryllium chloride (*M*/2; *M*/5) to potassium ferrocyanide solution, precipitation slowly sets in even at the room temperature.

Considering the above interesting facts for the reaction, it was thought worthwhile to carry out its detailed study. In this communication two aspects of the problem have been dealt with: (*i*) spectrophotometric study of the blue product formed on mixing the reactants and (*ii*) conductometric studies for the elucidation of the composition of the beryllium ferrocyanide.

EXPERIMENTAL

The beryllium chloride solution was obtained by adding a calculated amount of HCl to a weighed amount of beryllium oxide. After heating the resulting solution was filtered. A small portion of it was then estimated gravimetrically as BeO. Fresh solutions were prepared occasionally to avoid hydrolysis.

A concentrated solution of K_4FeCy_6 was prepared by dissolving recrystallised sample in doubly distilled water and the strength determined by titrating with potassium permanganate of known strength. The solution was stored in a dark-coloured bottle.

* Part III: *J. Sci. Ind. Res.*, 1959, **18B**, 643.

Spectrophotometric Determinations

Beckman DU spectrophotometer was used for the measurements. The cell was 1 cm corex type and the light source was a tungsten lamp.

Absorption experiments were performed after mixing 0.2c.c., 0.4c.c.....1.8c.c., 2.0c.c. 10^{-2} *M*-$BeCl_2$ with 10.0c.c. of 10^{-1} *M*-K_4FeCy_6, making the total volume to 12.0c.c. in each case. For one particular mixture, the absorption was noted for a number of wave lengths (between 350mμ and 500 mμ). It was observed that with increasing wave length the absorption value went on decreasing. At 350 mμ it was highest, so much that with mixtures containing large proportions of beryllium, the O.D. was near about 2. The wave lengths found suitable to work with were in the region 400 to 555 mμ. The absorption values at 460 and 500 mμ for the mixtures, kept overnight, are as shown in Table I

TABLE I

10^{-2}*M*-$BeCl_2$ added to 10c.c. of 10^{-1} *M*-K_4FeCy_6 (c.c.) ..	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
O.D. at 460 mμ ..	0.78	0.80	0.90	0.92	0.90	1.02	1.12	1.23	1.38	1.70
O.D. at 500 mμ ..	0.315	0.408	0.37	0.47	0.42	0.46	0.53	0.58	0.67	0.78

Table I evidently shows that the O.D. values increase with the increase in the concentrations of beryllium ions although irregularities are observed in certain cases. This may be due to the turbidity appearing in the mixtures on keeping overnight.

In view of the fact that it took some time for the blue colour to develop, the variation in the O.D. for three different solutions: (I) 0.5c.c., (II) 0.7c.c., (III) 0.9c.c. of 10^{-2} *M*-$BeCl_2$ in 10c.c. of 10^{-1} *M*-K_4FeCy_6 (total volume made to 12c.c.) at different time intervals were measured.

TABLE II

Time.	Wave length.	Optical density of solutions. (I).	(II).	(III).
3.45 p.m.	450 mμ	1.105	0.160	0.170
4.20	450	0.200	0.280	0.330
4.55	450	0.282	0.380	0.420
5.25	450	0.298	0.488	0.520
6.00	450	0.395	0.560	0.665
6.35	450	0.458	0.690	0.830

N.B. The solutions were mixed at 3.30 p.m.

Since the addition of a fairly concentrated solution of HCl to potassium ferrocyanide solution effected decomposition of the latter, resulting in the development of a blue colour, it was deemed necessary to carry out absorption experiments in presence of HCl. The three mixtures mixed were: (I) 0.5c.c., (II) 0.7c.c., and (III) 0.9c.c. of 10^{-1} *M*-HCl in 10.0c.c. of 10^{-1} *M*-K_3FeCy_6. The total volume was made to 12.0c.c. in each case.

TABLE III

Time.	Wave length.	Optical density of solutions. (I).	(II).	(III).
11.40 a.m.	450 mμ	0.125	0.24	0.345
12.0	450	0.190	0.32	0.40
12.30 p.m.	450	0.215	0.36	0.47
12.50	450	0.240	0.40	0.52
1.10	450	0.285	0.465	0.60

N. B. The solutions were mixed at 11 a.m.

In the preliminary experiments it was found that in a large number of cases the O.D. increased with increase in the concentration of Be^{2+} ions for mixtures kept overnight. To have a more precise idea of the influence of the concentration of the beryllium ions, measurements were made at different time intervals (40 minutes, 1½ hours and 2 hours) for five concentrations of beryllium ions in the mixture (0.1, 0.2, 0.5, 0.7 and 0.9c.c. of 10^{-2} *M*-$BeCl_2$ added to 10c.c. 10^{-1} *M*-K_4FeCy_6; total volume made to 12.0 c.c.).

TABLE IV

Time interval.	Wave length.	Optical density of solutions. (1)	(2)	(3)	(4)	(5)
50 mins	450mμ	0.037	0.150	0.200	0.280	0.315
1½ hrs.	450	0.050	0.194	0.270	0.365	0.420
2	450	0.055	0.260	0.298	0.480	0.520

Conductometric Titrations

The conductivity measurements were carried out by a W.T.W. conductivity bridge with a dip type conductivity cell. The beryllium chloride solution was neutralised with a few drops of strong caustic soda solution to increase the *p*H of the solution (*p*H 4.5). With concentrated solutions of the reactants, a white precipitate was obtained even at the room temperature, the supernatant liquid having a light greenish colour. This colour became darker with time and increasing temperature; volume correction (Davies, "The Conductivity of the Solutions"; Taylor, "A Treatise of Physical Chemistry, Chapter XIII) was made by multiplying the observed conductance by the factor $(V+v)/V$, where V refers to the volume of the reactant originally taken in the cell and v is the volume added. The titrations were carried out with different concentrations of the reactants at 30°, 60°, and 80°. Titrations with K_4FeCy_6 in the cell were not successful. Some of the results are summarised below.

TABLE V

$BeCl_2$ soln.	K_4FeCy_6 from the curve.	Ratio at the inflection point. Be^{2+} : $FeCy_6^{4-}$.
	Temp=30°±0.1°.	
10c.c. of *M*/2	12c.c. of *M*/5	2.081:1
10 *M*/5	9.6 *M*/5	10:9.66
9 *M*/5+1c.c. EtOH	9.0 *M*/5	1:1
	Temp.=60±0.1°.	
20 *M*/1000	2c.c. & 3.9c.c. of *M*/100	1:1 & 1:1.95
20 *M*/500	4 & 8.5 *M*/100	1:1 & 1:2.1
20 *M*/100	2 & 4.25 *M*/10	1:1 & 1:2.12
	Temp.=80±0.1°.	
20 *M*/1000	1.9 & 3.9 *M*/100	1.05:1 & 1:1.95
20 *M*/500	4.0 & 8.5 *M*/100	1:1 & 1:2.1

DISCUSSION

The variations in the optical densities of the various mixtures with time bring out two important facts regarding the nature of beryllium ferrocyanide reaction: (*i*) Decomposition of potassium ferrocyanide is a slow reaction and takes place with a definite velocity, (*ii*) the reaction is dependent on the concentration of beryllium ions, being faster at higher concentrations of beryllium. On plotting the O.D. against time (Table II), it was found that a break in the time—absorption curve occurred after a fixed period (90 minutes) for the different concentrations of Be^{2+}. The behaviour is rather significant and can be

explained by assuming that altogether different reactions take place in the early stages and thereafter. Further support to this viewpoint was forthcoming when curves were drawn between concentrations of beryllium ions and O.D. after 50 minutes, 90 minutes, and 120 minutes respectively (Table IV). There it is found that the curves for 120 minutes show an irregular behaviour and are quite different from those for the time periods 50 minutes and 90 minutes. From this it may be concluded that some sort of interaction of beryllium chloride and potassium ferrocyanide is also taking place simultaneously with the decomposition of the latter.

A comparison of the O.D. values in presence of Be^{2+} (Table II) and those in presence of varying amounts of 10^{-1} *M*-HCl (Table III) reveals that although the absorption values with hydrochloric acid are higher than those for Be^{2+} in the beginning, the development of blue colour is more rapid in presence of beryllium chloride than with solutions containing HCl (e.g. in approximately two hours the O.D. in presence of Be^{2+} increases from 0.17 to 0.58, whereas in presence of HCl it changes from 0.345 to 0.6). Moreover, on keeping the mixture for longer periods, solutions containing Be^{2+} gave very high values for O.D. when compared to solutions containing HCl (where some slight turbidity also appeared). These observations, combined with the fact that beryllium solution is only slightly acidic, indicate that the rapid and intense development of blue colour is not merely due to the hydrogen ions and that Be^{2+} ions are also involved in the reaction. The role of Be^{2+} in this reaction is not easy to see and appears to be a moot question. The hydrogen ions derived from the hydrolysis of the beryllium salts, combined with the slow aggregation of colloidal beryllium ferrocyanide (with a little beryllium hydroxide), may be responsible for the development of the blue colour from the slow decomposition of hydroferrocyanic acid in solution. The Prussian blue thus formed is likely to be adsorbed on the various sol particles of growing size, which increase the optical density of the solution over that of the solutions containing only HCl.

The spectrophotometric studies also show that the reaction can best be studied at 450 mμ and that the possibility of the reaction to be used as a micro test for detection of Be^{2+} cannot be completely ruled out.

Composition of Beryllium Ferrocyanide

Direct conductometric titrations with concentrated solutions of the reactants give a ratio $2Be^{2+}$:1 $FeCy_6^{4-}$ as well as a ratio of 1:1. This would mean the existence of two complexes having the formulas Be_2FeCy_6 and $K_2BeFeCy_6$. Since the appearance of the white precipitate at the room temperature on mixing beryllium chloride and potassium ferrocyanide takes some time, it is quite pobable that the compound Be_2FeCy_6 is formed with *M*/2 solution, whereas the complex $K_2BeFeCy_6$ is formed with dilute solutions (*M*/5).

Titrations carried out at temperatures 60° and 80° give two breaks. From these it may be concluded that besides the formation of the complex $K_2BeFeCy_6$, an addition complex, $K_2BeFeCy_6.K_4FeCy_6$, one mole of potassium ferrocyanide adsorbed per mole of the complex, is also formed.

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Studies on some Less Familiar Ferrocyanogen Complexes. Part V. Interactions of Be(II) and Cr(III) with Potassium Ferro- and Ferricyanides at 80° and their Composition by Amperometry

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Dilute solutions of beryllium nitrate and chromic chloride do not interact with potassium ferrocyanide at the ordinary temperature to form insoluble complexes. These, however, react at higher temperatures. The reactions have been studied at 80° employing the mercury pool as the reference electrode and potassium chlorate as the spporting electrolyte. Titrations between beryllium nitrate and potassium ferrocyanide have been carried out at 80°. Evidence for the formation of the complex $K_2Be_3{}^{II}(Fe^{II}Cy_6)_2$ has been obtained.

Conductometric and potentiometric titrations between chromic chloride and potassium ferrocyanide do not give satisfactory results, but the amperometric titrations, carried out at 80°, give evidence for the formation of the complex $KCr^{III}Fe^{II}Cy_6$. Amperometric studies, carried out under similar conditions, give evidence for the formation of the complex $Cr^{III}Fe^{III}Cy_6$ by the interaction of chromic chloride and potassium ferricyanide at 80°.

Amongst the metal ferrocyanogen complexes, beryllium and chromic compounds differ from other compounds of this class in as much as that their formation is favoured by high temperatures. As already reported in Part IV (this *issue*, p. 293) the reaction between beryllium chloride and potassium ferrocyanide took place at the room temperature only with the concentrated solutions of the reactants, whereas with the dilute solutions, a higher temperature (60-80°) was needed for its completion. Also in a previous communication (*J. Sci. Ind. Res.*, 1959, **18B**, 643) it was reported that besides the formation of a soluble complex at the room temperature, the reaction between chromic chloride and potassium ferrocyanide, when carried out a higher temperature (80°), resulted in the formation of a precipitate, highly gelatinous in character. Elucidation of the composition of both these complexes, employing physical methods, presented a number of difficulties.

Since the amperometric titrations offer a neat method for studying complex-ion formation with fairly dilute solutions, it was chosen for studying the composition of beryllium ferrocyanide. The investigations, however, presented many experimental difficulties. Firstly the beryllium chloride solution could not be used; secondly a suitable supporting electrolyte was to be found out because we failed to get a wave as reported in the literature (Kemula and Michallski, *Coll. Czech. Chem. Comm.*, 1933, **5**, 436) with beryllium nitrate alone; and finally a suitable reference electrode had to be selected to replace the calomel electrode (found unsuitable for working at 80°). The beryllium nitrate—potassium ferrocyanide reaction was therefore studied in detail with two aspects in view, viz., (*i*) polarographic investigation of beryllium nitrate and (*ii*) elucidation of the composition of beryllium ferrocyanide with the help of amperometric titrations.

The chromic chloride—potassium ferrocyanide reaction was first studied by employing potentiometric and conductometric titrations. Potentiometric titrations carried out at 80°, employing a $FeCy_6^{4-} \rightleftharpoons FeCy_6^{3-} + e$ couple at the platinum electrode, failed to provide sharp breaks in the titration curves, thereby furnishing little information regarding the composition of the complex. Although the conductometric titration method tried could supply some information regarding the composition of chromic ferrocyanide, it had its own

limitations. One factor mainly responsible for the limited applicability of the method in this particular case was the appreciable decrease in the mobility of the ions in the reaction mixture due to the highly gelatinous nature of the reaction product. The results on the preliminary experiments on conductometry at $80\pm0.1°$ at one particular concentration are given below.

$0.5M$-$CrCl_3$ in the cell.	$0.5M$-K_4FeCy_6 from the curve.	Ratio at the point of inflection. Cr^{3+}: $FeCy_6^{4-}$.
10 c.c.	9.8 c.c., 15.9 c.c.	1:1 ; 1:1.5
$0.5M$-K_4FeCy_6 in the cell.	$0.1M$-$CrCl_3$ from the curve.	
10 c.c.	5.1 c.c., 21.2 c.c.	1:10; 1:2.4

From the above it is evident that only the titrations carried out with $CrCl_3$ in the cell gave results of some importance (and that too in one stray case). On this basis the complex chromic ferrocyanide would have the probable formula $KCrFeCy_6$ and $KCrFeCy_6$.-$0.5K_4FeCy_6$ (an adsorption complex). Since fantastic results were obtained for the reverse titrations, in spite of the fact that typical titration curves were obtained, it was thought worthwhile to use a more suitable and at the same time accurate physical method for finding out its composition. The amperometric method was therefore also employed in these investigations.

EXPERIMENTAL

Beryllium nitrate solution was prepared by diluting A.R. sample in about 250c.c. of water and its strength, determined gravimetrically after weighing as BeO, was found to be $0.54M$. Chromic chloride (A.R.) was dissolved in double distilled water and its strength was determined iodometrically (W.Scott, "Standard Methods of Chemical Analysis", 1945, Vol. I, p. 288) after oxidising the solution to chromate by sodium peroxide. Potassium ferrocyanide and potassium ferricyanide (recrystallised) were also dissolved in double distilled water and the strength determined volumetrically. Concentrated solutions of potassium ferro- and ferricyanides were kept stored in dark bottles.

Polarographic Measurements

Fischer elecdropode in conjunction with a Multiflex galvanometer (Type MGF2) was employed for measurement of the current. The electrodes used were the dropping mercury electrode, S.C.E. (Fibre and dip types), and the mercury pool. Nitrogen gas, purified after passing through chromous chloride and pyrogallol, was used for maintaining the inert atmosphere. Thermostatic oil bath at $80\pm0.1°$ was used for temperature control. For studying the chromic chloride—potassium ferrocyanide reaction, potassium chloride was used as the supporting electrolyte and gelatin (0.01%) as the maximum suppressor.

Amperometric Titrations

Before carrying out the amperometric titrations between beryllium nitrate and potassium ferrocyanide, a number of polarograms of beryllium nitrate solutions in different supporting electrolytes (saturated $CaCl_2$; $CaCl_2$ saturated in $0.1M$-HCl; $KClO_4$ in $0.1M$-HCl; $0.1M$ $KClO_3$) and maximum suppressors (0.01% methyl red; 0.01% gelatin) employing S. C. E. (Fibre and dip types) as well as the mercury pool as reference electrodes were drawn. No waves were obtained with $Be(NO_3)_2$ solution without supporting electrolyte. From the different polarograms studied, it was found that the most suitable condition

for performing amperometric titrations was to apply a potential of about 1.90 volts at the dropping mercury electrode, using the mecury pool as the other half element with gelatin (0.01%) as the maximum suppressor and 0.1*M*-$KClO_3$ as the supporting electrolyte. Titrations were performed with $Be(NO_3)_2$ in the cell (direct) as well as K_4FeCy_6 in the cell (reverse). Since in the direct titrations the current went on continuously increasing, it was difficult to locate the null point; only one set of readings was taken. Better results were, however, obtained with the reverse titrations. The electrolyte solution was diluted to 20c.c. with potassium chlorate solution and 1c.c. of gelatin.

For studying the reaction between chromic chloride and potassium ferrocyanide, a polarogram of chromic chloride (using dip type S.C.E.) was taken. 0.1*M*-Chromic chloride (1c.c.) was taken in the cell and the total volume was made to 20c.c. with 1c.c. of gelatin solution and the rest, supporting electrolyte. The polarogram showed one irreversible wave (the second wave could not be realised since a hydrogen wave due to the hydrolysis of chromic ions was obtained in the vicinity of 1.4 volts) with $E_{\frac{1}{2}}$=0.88 volt. A potential of 1.0 volt was chosen for the titrations. Both direct ($CrCl_3$ in the cell) and the reverse (K_4FeCy_6 in the cell) titrations were tried. In the reverse titrations the current increased continuously on the addition of chromic chloride and the equivalence point could not be successfully located.

The amperometric titrations between chromic chloride and potassium ferricyanide were carried out at two different potentials. The direct titrations were carried out at 1.0 volt, whereas the reverse titrations were done at 0.0 volt (since in the case of potassium ferricyanide $E_{\frac{1}{2}}=\pm 0.2$ V, and a diffusion current for all negative values of the potential applied). Reverse titrations after applying a potential of 1.0 volt could not be satisfactorily performed due to the residual current.

The results are summarised in the following tables and typical curves are depicted in Figs. 1 to 3.

TABLE I

Potential applied=1.85 volts. Temp.=80±0.1°.

Vol. in the cell.	Vol. from the curve.	Ratio at the point of inflection.
	Direct titrations.	
0.154 *M*-$Be(NO_3)_2$	0.1 *M*-K_4FeCy_6.	Be^{2+} : $FeCy_6^{4-}$
0.6 c.c.	2.4 c.c.	1:2.6
	Reverse titrations.	
0.1*M*-K_4FeCy_6	0.1*M*-$Be(NO_3)_2$	
0.2 c.c.	0.2 c.c.	3:2
0.4	0.4	3:2
0.6	0.6	3:2

TABLE II

Potential applied=1.0 volt. Temp.=80±0.1°.

Vol. in the cell.	Vol. from the curve.	Ratio at the point of inflection.
0.1*M*-$CrCl_3$	0.1*M*-K_4FeCy_6	Cr^{3+} : $FeCy_6^{4-}$.
0.6 c.c.	0.60 c.c.	1:1
0.8	0.80	1:1
1.0	0.95	1:1

TABLE III

Vol. in the cell.	Vol. from the curve.	Ratio at the point of inflection.
0.1*M*-$CrCl_3$	0.1*M*-K_3FeCy_6	Cr^{3+} : $FeCy_6^{3-}$.
	Potential applied=1.0 volt. Temp.=80±0.1°.	
0.6 c.c.	0.40 c.c.	1.5 : 1
0.8	0.60	1.3 : 1
1.0	0.75	1.3 : 1
0.1*M*-K_3FeCy_6	0.1*M*-$CrCl_3$.	
	Potential applied=0.0 volt. Temp.=80±0.1°.	
0.4	0.4	1 : 1
0.6	0.6	1 : 1
1.0	0.8	1.1 : 1

DISCUSSION

Amperometric titrations with beryllium nitrate in the cell did not provide typical amperometric curves. Here the current went on increasing due to hydrolysis. The probable equivalence point, however, gave a ratio of Be^{2+}: $FeCy_6^{4-}$ as 1:2.6, showing thereby the great adsorptive capacity of the complex $K_2Be^{II}Fe^{II}Cy_6$ for the ferrocyanide ions. The results support the earlier work (Part IV) where the existence of adsorption complexes like $K_2Be^{II}Fe^{II}Cy_6$. K_4FeCy_6 was envisaged on the basis of direct conductometric titrations.

The reverse titrations, potassium ferrocyanide in the cell, gave the ratio Be^{2+}: $FeCy_6^{4-}$ as 3:2, thereby indicating the formation of the complex $K_2Be_3^{II}(Fe^{II}Cy_6)_2$. Further, the amperometric titrations were of extra advantage in as so far as they could supply information regarding the composition of the compound formed when beryllium nitrate is added to potassium ferrocyanide—a fact which could be investigated on the basis of conductometric titrations.

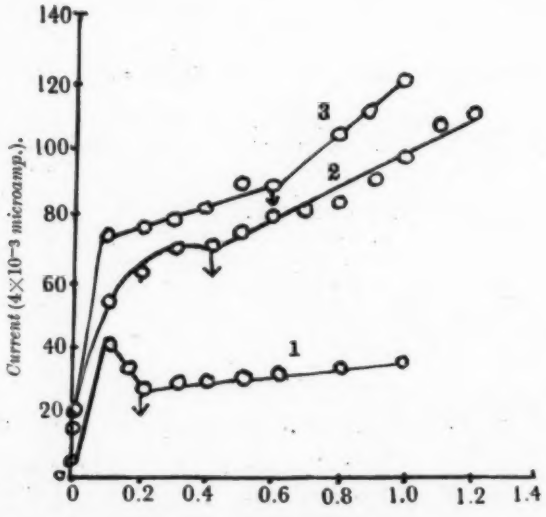

FIG. 1. Curves 1-0.2 c.c. 2-0.4 c.c. and 3-0.6 c.c. of 0.1 *M*-K_4FeCy_6 in the cell.

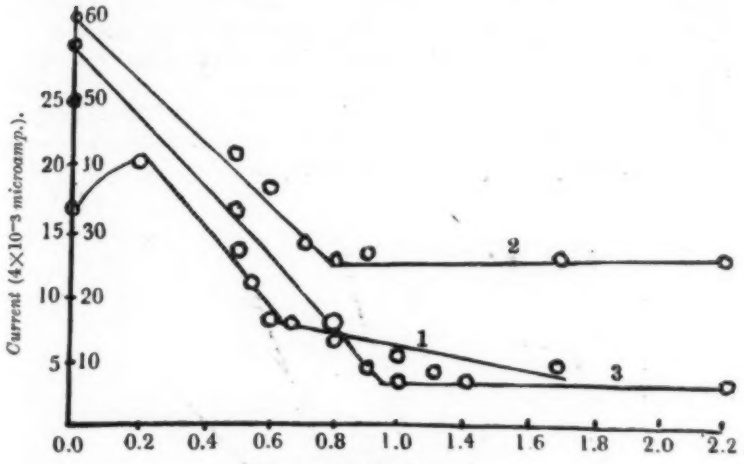

FIG. 2. Curves 1-0.6 c.c., 2-0.8 c.c., and 3-1.0 c.c. of M-$CrCl_3$ in the cell.

Summing up the studies on the composition of beryllium ferrocyanide, it may be said that the complex has got the composition $K_2Be^{II}Fe^{II}Cy_6$ and $K_2Be_3^{II}$ $(Fe^{II}Cy_6)_2$, depending on the mode of mixing the reactants. When potassium ferrocyanide is added to beryllium, a compound with the formula $K_2Be^{II}Fe^{II}Cy_6$ is obtained, whereas on adding beryllium nitrate to potassium ferrocyanide, a complex having the formula $K_2Be_3(FeCy_6)_2$ is formed. Moreover, the compound $K_2BeFeCy_6$ shows a great tendency to adsorb the ferrocyanide ions and hence under these conditions the reaction cannot be employed for the estimation of beryllium, as reported recently (Part IV, *loc. cit.*).

Chromic Ferro-and Ferricyanide Complexes

The results on amperometric titrations between chromic chloride and potassium ferro-and ferricyanide solutions provide ample proof regarding the composition of the precipitates obtained by their interaction at 80°. As already pointed out, the potentiometric and conductometric titration methods failed to supply the required information about their composition.

The curves for the direct titrations between chromic chloride and potassium ferrocyanide are typical in nature. Initially the current goes on decreasing with the removal of chromic ions due to the precipitation of chromic ferrocyanide, but after complete precipitation the current is almost constant in view of the nonreducibility of potassium ferrocyanide at the dropping mercury electrode. The ratio 1:1 for the reactants found on the basis of these titrations would point towards the composition $KCr^{III}Fe^{II}Cy_6$ for the complex.

The amperometric titrations carried out between chromic chloride and potassium ferricyanide at 1.0 volt gave ratios Cr^{3+} : $FeCy_6^{3-}$ as 1.3:1 and 1.5:1. Such ratios although do not provide any precise information regarding the composition of chromic ferricyanide, it may be said that a compound having the composition $Cr^{III}Fe^{III}Cy_6$ is formed with chromic ions adsorbed on it. The reverse titration proved, however more fruitful and gave a ratio 1:1 for the reactants. An intresting point regarding the shape of the amperometric

titration curves in this case is worth mentioning. It was found that the current values became negative with successive addition of chromic chloride from the burette to potassium ferricyanide solution. In order to explain this behaviour one has to take into consideration the hydrolytic nature of the complex. It is quite probable that chromic ferricyanide hydrolyses to yield chromic hydroxide and the negative current may be due to some of the hydroxyl ions present in the reaction mixture. Separate experiments performed with buffers (*p*H 8) and alkali solutions gave negetive current at 0.0. volt.

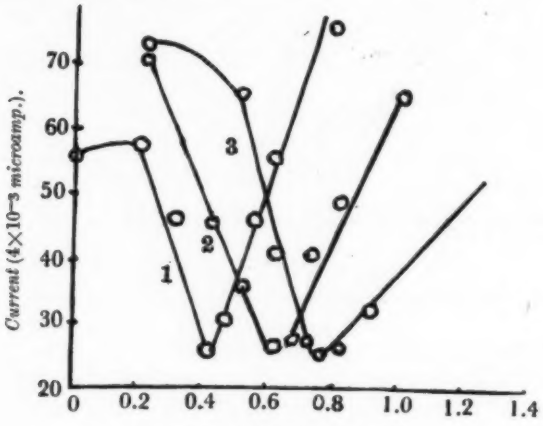

FIG. 3. Curves 1-0.6 c.c., 2-0.8 c.c. and 3-1.0 c.c. of 0.1 *M*-$CrCl_3$ in the cell.

Thanks are due to Prof. M.O. Farooq, lately Head of the Chemistry Department, for his interest in the work.

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Studies on some Less Familiar Ferrocyanogen Complexes. Part VI. Investigation on the Ferrocyanogen Complexes of Cu(I), Ti(III and IV), Cr(II), and Mn(III) in the Light of Redox Potential

Wahid U. Malik

The ferrocyanogen complex of Cu (I), Ti (III), Ti (IV), Cr (II), and Mn (III) have been studied by amperometry. The results have been interpreted in the light of the oxidation-reduction potential existing in the reactions between Cu(I), Ti(III) or Cr(II) and potassium ferricyanide and that between Mn (III) and potassium ferrocyanide. The composition of cuprous ferrocyanide (white in colour) has been found to be $K_2Cu^{I}\ Fe^{II}\ Cy_6$, whereas the products obtained by interaction of cuprous chloride and potassium ferricyanide may be represented by the formula $K_2Cu^{II}\ Fe^{II}\ Cy_6$ and $KCu_2{}^{I}\ Fe^{III}\ Cy_6$. The titanium complexes of the following compositions have been obtained: $KTi^{III}\ Fe^{II}\ Cy_6$; $Ti_4{}^{III}\ (Fe^{II}\ Cy_6)_3$; $Ti^{IV}\ Fe^{II}\ Cy_6$ (for titanous chloride-potassium ferricyanide reaction). For the chromous chloride—potassium ferricyanide reaction complexes of the type $Cr_3{}^{II}\ (Fe^{III}\ Cy_6)_2$ and $K_2Cr^{II}\ Fe^{II}\ Cy_6$ are obtained depending on the mode of mixing of the reactants.

The Mn (III)—potassium ferrocyanide reaction, besides providing evidence of the existence of the redox potential in the system:

$$Mn^{3+} + FeCy_6{}^{4-} \rightleftharpoons Mn^{2+}FeCy_6{}^{3-}$$

also shows the presence of the complex anion $Mn\ (SO_4)^{2-}$ in the reaction mixture. The latter fact is also supported from the amperometric titrations between Mn (III) and potassium ferricyanide. The various complexes formed are $Mn^{III}\ Fe^{III}\ Cy_6$, $KMn^{III}\ Fe^{II}\ Cy_6$, and $Mn^{III}\ Fe^{III}\ Cy_6$ (for the Mn^{III}—ferricyanide reaction).

The problem of the existence of redox potential in the system comprising the interaction of metal ions and alkali ferro-and ferricyanides has attracted little attention of the workers in this field. Attention to this fact was first drawn by Davidson (*J. Chem. Ed.*, 1937, **14**, 238, 277), who on the basis of some preliminary experiments demonstrated the influence of the redox potential in the system:

$$Fe^{3+} + FeCy_6{}^{4-} \rightleftharpoons Fe^{2+} + FeCy_6{}^{3-}$$

on the formation of Prussian blue. Since then nothing has been done to record such influences by investigating the composition of metal ferrocyanogen complexes.

Of the many metal ions, which could be studied from this aspect, a few typical ones, namely Cu(I), Ti(III and IV), Cr (II), and Mn (III) were selected for the present investigations.

Preliminary experiments, performed on mixing varying proportions of equimolecular solutions of cuprous chloride and potassium ferrocyanide showed, that the precipitate obtained with an excess of the latter reactant was reddish brown in colour, whereas that obtained in presence of excess of cuprous chloride was white. Also with excess of potassium ferrocyanide the supernatant liquid turned to green and finally to blue due to the probable formation of Prussian blue by slow decomposition of hydroferrocyanic acid. As for the interaction of cuprous chloride and potassium ferricyanide, brown-coloured compounds were obtained in all cases, irrespective of the excess of either of the reactants although with excess of ferricyanide, the colour was quite dark, approaching to black. Here also the supernatant liquid turned green on keeping.

In the case of Ti(III)—potassium ferrocyanide reaction, a dark yellow precipitate was

obtained with the excess of titanous ions whereas with an equimolecular proportion of the reactants and with excess of potassium ferrocyanide, an orange-coloured precipitate was obtained. Further, in test tubes containing large excess of potassium ferrocyanide, a blue colour developed on the surface of the precipitate on keeping. For Ti(III) and potassium ferricyanide interaction, an orange-coloured precipitate (similar to that of titanous ferrocyanide) was obtained with excess of the former, but for mixtures containing equimolecular proportions of the reactants or excess of potassium ferricyanide, a dark brown precipitate was obtained. Ti(IV) does not give any precipitate with potassium ferricyanide in the cold and on heating only a slight yellow turbidity appears. It, however, reacts with potassium ferrocyanide. Here too the colour of the precipitate depended on the proportion of the reactants mixed. With excess of titanic ions, a chocolate-coloured precipitate was obtained, whereas on mixing equimolecular proportion of the reactants a dark brown precipitate was formed. Addition of excess of potassium ferrocyanide resulted in the formation of a yellowish brown precipitate.

The interaction of Cr(II) with potassium ferro-and ferricyanides remained obscure so far. The Cr(II)—ferrocyanide reaction was first studied in our laboratory (Malik and Abubacker, *Z. anorg. Chem.*, 1959, **301**, 343, 350). These studies were further extended so as to include the interaction of Cr (II) and potassium ferricyanide. The reaction product was dirty yellow with excess of ferricyanide, but it was yellowish green with chromous chloride.

The reaction between Mn(III) and alkali ferro-and ferricyanides has hitherto not been investigated and presents a number of complexities. The manganic ion, unlike Cu (I), Cr(II), Ti (III), etc., is fairly ustable in the aqueous solution and changes of the type :

$$2Mn^{3+} + 2H_2O \rightleftharpoons MnO_2 + Mn^{2+} + 4H^+$$

are known to take place in solution. Further, the possibility of the reaction $2Mn^{3+} \rightleftharpoons Mn^{2+} + Mn^{4+}$ cannot be ruled out. Stability is usually obtained by changing the simple manganic ion into the orthophosphate, potassium manganicyanide and the alums. It is also observed that if the oxidation of Mn(II) is carried out in concentrated hydrochloric acid and sulphuric acid solutions, it does not contain pure Mn(III), but is mixed with chloro-complexes of intermediate composition (Ibers and Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 4744) or the sulphato-complexes of the type $Mn(SO_4)_2^-$ (Ubbelhode, *J. Chem. Soc.*, 1935, 1605). Mn(III) solution, prepared by the method recommended by Ubbelhode, was, however, used to study the ferrocyanogen complexes in spite of the limitations encountered in obtaining a pure manganic sulphate solution.

EXPERIMENTAL

Cuprous chloride was obtained by reducing cupric chloride by copper turnings in presence of HCl (conc.). To the colorless solution, thus obtained, excess of water was added to form the white precipitate. It was washed with ethanol and then with ether, and finally dried in a vacuum desiccator over lime. The solution was prepared by dissolving 1.98 *g.* of the dried substance in 100 c.c. 0.1*N*-KCl solution. It was kept under a layer of paraffin to avoid oxidation. The strength of the solution was determined by titrating against 0.1*M* ammonium thiocyanate, using ferric alum as the indicator (Malik *et al.*, *Z. anorg. Chem.*, 1959, **299**, 322). The strength was found to be 0.098*M*.

To a 12.5% titanous chloride solution (250c.c.) in 15% HCl (B.D.H., 2g.) spectroscopically pure titanium metal was added. Hydrochloric acid gas was then passed in the solution for about 10 minutes. The mixture was heated to dissolve the titanium metal.

HCl gas was then passed for about an hour while keeping the solution in a freezing mixture. On keeping for some time, violet crystals of titanous chloride appeared. The crystals were washed with air-free double distilled water and dissolved in 15% HCl solution (these were also found to be soluble in absolute etthanol). The strength was determined by titrating against 0.1*N*-$KMnO_4$ (Scott, "Standard Methods of Analysis", 5th ed., p. 984). The strength was found to be 0.087*M*.

12.5% $TiCl_4$ in 15% hydrochloric acid (B.D.H.) was employed for preparing the solution. The strength was determined by precipitating titanium as hydroxide and weighing as TiO_2 (Scott, *loc. cit.*, p. 982). The strength was found to be 0.093*M*.

Chromous chloride solution was obtained after reducing chromic chloride with zinc and HCl. The method recommended by Balth and Baeler (*J. Amer. Chem. Soc.*, 1936, **58**, 1474) with a slight modification was followed (Malik and Abubacker, *loc. cit.*). The solution was stored in a Stone-type bottle (Stone, *Anal. Chem.*, 1948, **20**, 747) and it remained stable for many weeks. Since the strength of chromous chloride had to be determined and checked occasionally during the course of experiments, the method of Zintl and Rienacker (*Z. anorg. Chem.*, 1927, **161**, 374, 385; 1927, **168**, 97), using copper sulphate or potassium dichromate, was replaced by a quicker method. 0.1*N*-$KMnO_4$ (50c.c.), acidified with 2*N*-H_2SO_4 (15c.c.) was taken in a 100 c.c. beaker and covered with a layer (about 0.5c.c. thick) of kerosine. A chromous chloride solution (2c.c.) was then transferred to the permanganate, keeping the tip of the burette under the layer of kerosine. The mixture was stirred and kept aside for 5 minutes to ensure complete oxidation of Cr(II) and the excess of permanganate titrated against 0.1*N* ferrous ammonium sulphate using a Tinsley potentiometer (type 387B). The strength of chromous chloride then determined was 0.245*N*.

The manganic sulphate solution was prepared by the method recommended by Ubbelhode (*loc. cit.*) to avoid formation of higher oxides in the solution. It was found safer to add a little more sulphuric acid than that recommended by Ubbelhode. Attempts to prepare solutions of higher concentrations than 0.07*N* met with failure. The strength was determined by titrating against ferrous ammonium sulphate of known strength. The end point was detected by the change in colour from light green to yellowish green. It was further confirmed by titrating potentiometrically against hydrogen peroxide. A jump in potential of 0.35 volt was observed at the end point by the addition of a single drop of the titrant.

The potassium ferro- and ferricyanide solutions were prepared and stored as described in Part V (this *issue*, p. 297), Their strength was determined by titrating against potassium permanganate (for the ferrocyanide) and iodometrically (for the ferricyanide).

Amperometric Titrations

Polarographic measurements were carried out with a Fischer elecdropode in conjunction with a Multiflex galvanometer of type MGF2 (sensitivity, 1: 10; 4×10^{-9} ampere per division) against a S.C.E. 0.1*M*-KCl [(4*N*-HCl for Ti(III)] and $CaCl_2$ in HCl for Ti(IV) were used as the supporting electrolyte and gelatin (0.01%) as the maximum suppressor. For studying the manganic sulphate reaction, the sulphuric acid present in the solution was enough to be used as the supporting electrolyte. Purified nitrogen gas was passed in the cell for maintaining an inert atmosphere. Before carrying out the titration, polarograms for the reduction of various metal ions were taken for the following mixtures:

(*i*)	0.6c.c. of 0.098*M*-Cu_2Cl_2	+	1c.c. gelatin	+18.4c.c. of 0.1*M*-KCl.
(*ii*)	0.6c.c. of 0.087*M*-$TiCl_3$	+	Do	+18.4 of 4*N*-HCl.
(*iii*)	0.6c.c. of 0.093*M*-$TiCl_4$	+	Do	+18.4 of $CaCl_2$ in HCl.
(*iv*)	0.5c.c. of 0.245*M*-$CrCl_2$	+	Do	+18.5 of 0.1*M*-KCl.
(*v*)	10c.c. of 0.068*M*-$Mn_2(SO_4)_3$	+	Do	+11c.c. water.

The $E_{\frac{1}{2}}$ values from the curves were found to be 0.23V (Cu_2Cl_2), 0.12V ($TiCl_3$), 0.14V ($TiCl_4$), and 1.51V [$Mn_2(SO_4)_3$]. For Cr(II) the anodic wave was not reversible.

The potentials to be applied for the amperometric titrations were found from the plateau of the polarograms. These were: 0.6V (Cu_2Cl_2), 0.4V ($TiCl_4$), 0.2V ($CrCl_2$), 0.4V $Mn_2(SO_4)_3$]. For Ti (III), titrations were carried out at 0.0 volt. The latter potential was also applied in the case of Cu(I)—K_3FeCy_6 titrations.

The results are summarised in the following tables. A few typical amperometric titration curves are depicted in Figs. 1 to 5.

TABLE I

Cu(I)—*ferrocyanide reaction.*

Potential applied=0.6 volt. Temp.=30±0.1°.

Vol. in the cell. 098*M*-Cu_2Cl_2.	Vol. from the curves. 0.1*M*-K_4FeCy_6.	Ratio at the inflection point. Cu_2Cl_2 : K_4FeCy_6.
0.2 c.c.	0.2 c.c.	1:1
0.4	0.4	1:1
0.6	0.6	1:1
0.1*M*-K_4 $FeCy_6$.	0.098*M*-Cu_2Cl_2.	
0.2 c.c.	0.22 c.c.	1:1
0.4	0.39	1:1
0.6	0.61	1:1

TABLE II

Cu(I)—*ferricyanide reaction.*

Potential applied=0.0 volt. and 0.6 volt. Temp.=30±0.1°.

*Vol. in the cell. 0.098 *M*-Cu_2Cl_2.	Vol. from the curves. 0.155*M*-K_3FeCy_6.		Ratio at the inflection point. Cu_2Cl_2 : K_3FeCy_6.	
	0.0 volt.	0.6 volt.	0.0 volt.	0.6 volt.
0.2 c.c.	0.25 c.c.	0.1, 0.25c.c,	1:1.8	1:1;1:2
0.4	0.50	0.30, 0.60	1:2.0	1:0.94;1:11.94
0.5	0.60	0.39, 0.72	1:1.9	1:1; 1:1.90

* 0.2 c.c, 0.5 c.c. and 0.6 c.c. taken when applying 0.6 volt.

0.155*M*-K_3FeCy_6.	0.098*M*-Cu_2Cl_2.			
	0.0 volt.	0.6 volt.		
0.2 c.c.	0.15 c.c.	0.15,0.28 c.c.	1:2.1	1:2.1:1
0.4	0.30	0.3, 0.60	1:2.1	1:2.1;1:1.15
0.6	0.50	0.52,0.82	1:1.9	1:1.8;1:1.16

TABLE III

Ti(III)—*ferrocyanide reaction.*

Potential applied=0.0 volt. Temp.=30±0.1°.

Vol. in the cell. 0.087*M*-$TiCl_3$.	Vol. from the curves. 0.1*M*-K_4FeCy_6.	Ratio at the inflection point. $TiCl_3$: K_3FeCy_6.
0.3c.c.	0.22c.c.	1.0 : 0.85
0.6	0.42	1.0 : 0.80
1.0	0.65	1.0 : 0.75
0.1*M*-K_4FeCy_6.	0.0875 *M*-$TiCl_3$.	
0.3 c.c.	0.34 c.c.	1:1
0.6	0.70	1:1
1.0	1.18	1:1

TABLE IV

Ti(IV)-*ferricyanide reaction.*

Potential applied=0.4 volt. Temp.=30±0.1°.

Vol. in the cell.	Vol. from the curves.	Ratio at the inflection point.
0.087*M*-$TiCl_3$.	0.155*M*-K_3FeCy_6.	$TiCl_3$: K_3FeCy_6.
0.3c.c.	0.20c.c.	1:1.20
0.6	0.35	1:1.04
1.0	0.05	1:1.00
0.155*M*-K_3FeCy_6	0. 087 *M*-$TiCl_3$.	
0.4	0.66	1:1.2
1.0	1.9	1:1.0

TABLE V

Ti(IV)-*ferrocyanide reaction.*

Potential applied=0.4 volt. Temp.=30±0.1°.

Vol. in the cell.	Vol. from the curves.	Ratio at the inflection point.
0.093*M*-$TiCl_4$.	0.01*M*-K_4FeCy_6.	$TiCl_4$: K_4FeCy_6.
0.3c.c.	No definite break	—
0.6	0.6c.c.	1:1.1
1.0	0.9	1:1.0
0.1*M*-K_4FeCy_6.	0.093*M*-$TiCl_4$.	
0.4	0.4	1:1.07
0.6	0.6	1:1.07
1.0	1.1	1.100

TABLE VI

Cr(II)-*ferricyanide reaction.*

Potential applied=0.2 volt. Temp.=30±0.1°.

Vol. in the cell.	Vol. from the curves.	Ratio at the inflection point.
0.245*M*-$CrCl_2$.	0.1*M*-K_3FeCy_6.	$CrCl_2$: K_3FeCy_6.
0.4c.c.	0.46 c.c.	2.04:1
0.8	0.90	2.04:1
1.2	1.45	2.02:1
0.1*M*-K_3FeCy_6.	0.245*M*-$CrCl_2$.	
0.5	0.30	1.47:1
1.0	0.55	1.35:1
1.5	0.95	1.59:1

TABLE VII

Mn (III)-*ferrocyanide reaction.*

Potential applied=0.4 volt. Temp.=30±0.1°.

Vol. and conc. in the cell.	Vol. from the curves.	Ratio at the inflection point.
Mn(III).	0.2*M*-K_4FeCy_6.	Mn^{3+}: $FeCy_6^{4-}$.
20c.c. 0.0243 *M*	1.24 c.c.	1:1
20 0.016	0.80	1:1
20 0.020	1.09	1:1
K_4FeCy_6.	0.04*M*-Mn (III).	
20 c.c. 0.002	2.5 c.c.	2.05:1
20 0.0025	2.6	2.06:1
20 0.0030	3.9	2,00:1

TABLE VIII

Mn (III)-*ferricyanide reaction.*

Potential applied = 0.4 volt. Temp. = 30±0.1°

Vol. and conc. of Mn (III) in the cell.	Vol. of 0.2*M*-K_3FeCy_6 from the curves.	Ratio at the inflection point. Mn^{3+}: $FeCy_6^{3-}$
20 c.c. ; 0.0133*M*	1.3 c.c.	1:1
20 ; 0.0166	1.7	1.02:1
20 ; 0.0200	2.0	1:1

DISCUSSION

Cu (I) *Ferro- and Ferricyanides*

For the interaction of cuprous chloride and potassium ferrocyanide, the combining ratio of the reactants comes out to be 1:1, thereby pointing towards the formation of the complex $K_2Cu_2^{I}Fe^{II}Cy_6$ (white in colour).

The interaction of cuprous chloride and potassium ferricyanide presents a number of interesting features. Considering the oxidation potentials of the systems:

$$FeCy_6^{4-} \rightleftharpoons FeCy_6^{3-} + e \ (-0.44V) \quad \text{and} \quad Cu^{+} \rightleftharpoons Cu^{2+} + e \ (0.17V),$$

the equilibrium constant of the reaction:

$$Cu^{+} + FeCy_6^{3-} \rightleftharpoons Cu^{2+} + FeCy_6^{4-}, \quad K = Cu^{2+} \times FeCy_6^{4-} / Cu^{+} \times FeCy_6^{3-} = 3.7. \times 10^{4}.$$

It would mean that during the interaction of cuprous chloride and potassium ferricyanide, a considerably large amount of cuprous chloride is oxidised to the cupric state and consequently the ferricyanide is reduced to the ferrocyanide. Under these conditions the reaction would be:

$$Cu_2Cl_2 + 2\ K_3FeCy_6 + 2\ KCl = 2\ CuCl_2 + K_4FeCy_6$$
$$2CuCl_2 + 2\ K_4FeCy_6 = 2\ K_2CuFeCy_6 + 4KCl$$

The overall reaction would be

$$Cu_2Cl_2 + 2\ K_3FeCy_6 = 2\ K_2Cu^{II}\ Fe^{II}\ Cy_6 + 2KCl.$$

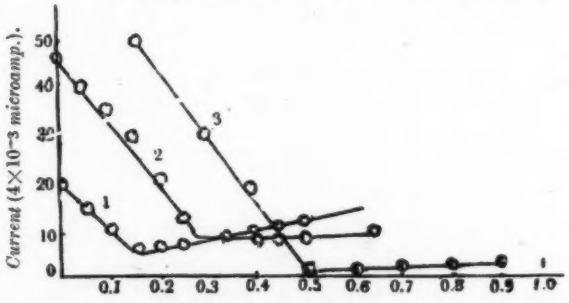

FIG. 1. Curves 1-0.2 c.c. 2-0.4 c.c. and 3-0.6 c.c. of 0.155*M*-K_3FeCy_6 in the cell.

Results on amperometric titrations support the above mechanism, where a ratio Cu_2Cl_2: K_3FeCy_6 as 1:2 for both reverse and direct titrations, carried out at 0.0 and 0.6 volt, is obtained. A ratio of 1:1 is also obtained for the second break from the curve at 0.6 volt. From this it may be concluded that some of the cuprous chloride reacts with potassium ferricyanide to give cuprous ferricyanide:

$$Cu_2Cl_2 + K_3FeCy_6 = KCu_2^{I}\ Fe^{III}\ Cy_6 + 2KCl.$$

It therefore amounts to the fact that the reaction between cuprous chloride and potassium ferricyanide is not simply an oxidation-reduction but proceeds with the formation of cupric ferrocyanide together with a little amount of cuprous ferricyanide. Incidentally, the reaction is just the reverse of that for the formation of Prussian blue, where the equilibrium constant of the reaction:

$$Fe^{3+} + FeCy_6^{4-} \rightleftharpoons FeCy_6^{3-} + Fe^{2+}$$

is of the order 10^5 and that the formation of ferric ferrocyanide is a slow reaction.

Further confirmation for this reaction between potassium ferricyanide and cuprous chloride was sought for carrying out the amperometric titrations between cupric chloride and potassium ferro- and ferricyanides. Here it was found that the ratio $CuCl_2$:K_4FeCy_6 or K_3FeCy_6 is 3:2. For this ratio, the composition of cupric ferrocyanide would be $Cu_3^{II}(Fe^{III}Cy_6)_2$. Formation of a compound with this composition is, however, not met with when considering the interaction of cuprous chloride and potassium ferricyanide.

Ti(III *and* IV) *Ferro- and Ferricyanides*

The reverse titrations give a ratio 1:1 for the reactants, pointing towards the formation of the complex titanous ferrocyanide of composition $KTi^{III}Fe^{II}Cy_6$. For the direct titrations concordant values are not obtained, but these may be approximated to 1:0.75. Here the composition of the complex would be $Ti_4^{III}(Fe^{II}Cy_6)_3$ according to the stiochiometric equation:

$$4TiCl_3 + 3K_4FeCy_6 = Ti_4(FeCy_6)_3 + 12\,KCl.$$

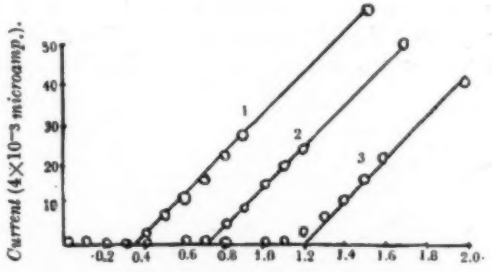

FIG. 2. Curves (1) 0.3 c.c., (2) 0.6 c.c. and (3) 1.0 c.c. of 0.1*M*-K_4FeCy_6 in the cell.

That the composition of the complex formed by the interaction of titanous chloride and potassium ferricyanide can be simply represented by $Ti^{III}Fe^{III}Cy_6$ (Ti^{3+} : $FeCy_6^{3-}$ as 1:1) appears to be highly improbable in view of the oxidation potentials existing in the system. The potential values of $FeCy_6^{4-} \rightleftharpoons FeCy_6^{3-} + e$ and $Ti^{3+} \rightleftharpoons Ti^{4+} + e$ are -0.44V and -0.6V respectively. The equilibrium constant of the reaction:

$$Ti^{3+} + FeCy_6^{3-} \rightleftharpoons Ti^{4+} + FeCy_6^{3-}$$

would be 2.7×10^6.

The large value of K in this case also points towards the fact that the titanous ions are oxidised to titanic ions during the course of the reaction and $Ti^{IV}Fe^{II}Cy_6$ is formed. The formation of this complex would be a ratio 1:1 for the reactants and this is what has been obtained from the amperometric titrations. It appears that the reaction takes place in two stages:

$$TiCl_3 + K_3FeCy_6 + KCl = K_4FeCy_6 + TiCl_4$$
$$TiCl_4 + K_4FeCy_6 = TiFeCy_6 + 4\,KCl$$

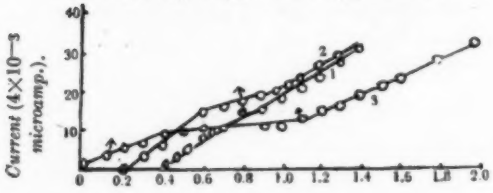

FIG. 3. Curves (1) 0.4 c.c., (2) 0.6 c.c., (3) 1.0c.c. of 0.1*M*-K_4FeCy_6 in the cell.

The view that titanic ferrocyanide is formed by the interaction of titanous chloride and potassium ferricyanide finds support in the titration between potassium ferrocyanide and titanic chloride. The ratio for the interaction of the two reactants again comes out to be 1:1, providing a definite proof for the formation of the complex $Ti^{IV}Fe^{II}Cy_6$.

Cr(II)-*Ferricyanide*

The insoluble complex (yellowish green in colour), formed by the interaction of chromous chloride and potassium ferricyanide may, take place according to the stiochiometric equations:

(*i*) $K_3FeCy_6 + CrCl_2 = KCrFeCy_6 + 2\,KCl$

(*ii*) $2\,K_3FeCy_6 + 3\,CrCl_2 = Cr_3(FeCy_6)_2 + 6\,KCl$

The results of the reverse amperometric titrations point towards the formation of the complex $Cr_3^{II}(Fe^{III}Cy_6)_2$ (Cr^{2+} : $FeCy_6^{3-}$ as 3:2 approx.). No clue regarding the existence of complex $KCr^{II}Fe^{III}Cy_6$, however, is forthcoming on the basis of amperometric titrations.

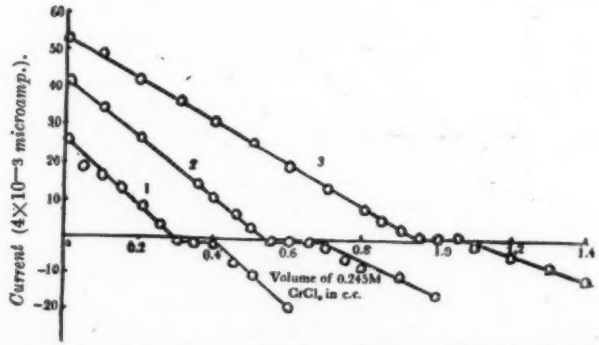

FIG. 4. Curves (1) 0.5 c.c., (2) 1.0 c.c., (3) 1.5 c.c. of 0.1*M*-K_3FeCy_6 in the cell

This reaction is also worth considering from the viewpoint of redox potential existing in the system. The equilibrium constant of the reaction:

$$Cr^{2+} + FeCy_6^{3-} \rightleftharpoons Cr^{3+} + FeCy_6^{4-}$$

is 2.5×10^{14} ($FeCy_6^{4-} \rightleftharpoons FeCy_6^{3-} + e = -0.44V$; $Cr^{2+} \rightleftharpoons Cr^{3+} + e = 0.41V$),
It would mean that during the interaction of chromous chloride and potassium ferricyanide a considerably large amount of chromous chloride would be oxidised to chromic state and the ferricyanide is reduced to the ferrocyanide. Due to the existence of

oxidation-reduction potential in the reaction, the following reactions may be expected to take place:

$$(i)\quad CrCl_2+K_3FeCy_6+KCl = CrCl_3+K_4FeCy_6$$
$$(ii)\quad CrCl_2+K_4FeCy_6 = K_2CrFeCy_6+2KCl$$
$$(iii)\quad CrCl_2+K_2CrFeCy_6 = Cr_2FeCy_6+2\,KCl$$
$$(iv)\quad CrCl_3+K_4FeCy_6 = KCrFeCy_6+3\,KCl$$

Of these the last reaction is quite slow at the ordinary temperature. The faster reaction between chromous chloride and potassium ferrocyanide (so also between chromous chloride and potassium ferricyanide) is more likely to occur. The first three reactions point towards the formation of complexes $K_2Cr^{II}\,Fe^{II}\,Cy_6$ and $Cr_2^{II}Fe^{II}Cy_6$ and these could be formed when the reactants are mixed in the ratios Cr^{2+} : $FeCy_6^{3-}$ as 2:1 and 3:1 respectively. The results on direct amperometric titrations give evidence for the complex having the formula $K_2Cr^{II}\,Fe^{II}\,Cy_6$.

Mn(III)—*Ferro- and Ferricyanides*

The possible reaction between manganic sulphate and potassium ferrocyanide may be represented as follows:

$$(i)\quad 2Mn_2(SO_4)_3+3K_4FeCy_6 = Mn_4(FeCy_6)_3+6K_2SO_4$$
$$(ii)\quad Mn_2(SO_4)_3+2K_4FeCy_6 = 2KMnFeCy_6+3K_2SO_4$$
$$(iii)\quad Mn_2(SO_4)_3+2K_4FeCy_6 = 2MnSO_4+2K_3FeCy+K_2SO_4$$

followed by either

$$(iv)\quad Mn_2(SO_4)_3+2K_3FeCy_6 = 2Mn^{III}\,Fe^{III}\,Cy_6+3K_2SO_4$$

or

$$(v)\quad 2MnSO_4+2K_3FeCy_6 = 2KMn^{II}\,Fe^{III}\,Cy_6+2K_2SO_4$$

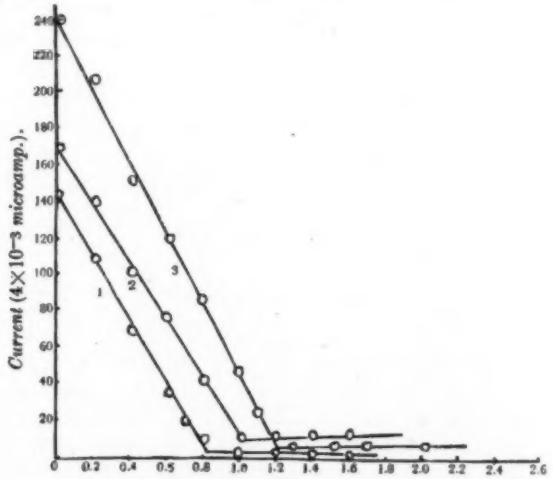

FIG. 5. Curves (1) 4 c.c., (2) 0.8 c.c., and (3) 9.6 c.c. of 0.05*M* Mn(III) in the cell.

The reactions (*i*) and (*ii*) would take place when manganic sulphate and potassium ferrocyanide combine in the ratio 2:3 and 1:2 respectively, whereas reactions (*iii*) and (*iv*) combined would give the ratio 1:1 and (*iii*) and (*v*) combined would give the ratio 1:2.

The amperometric titrations, when carried out with Mn (III) in the cell, give a ratio 1:1, pointing towards the formation of the complex $Mn^{II}Fe^{II}Cy_6$, the overall reaction taking place being

$$2Mn_2(SO_4)_3+2K_4FeCy_6 = 2Mn^{III}\,Fe^{III}\,Cy_6+2MnSO_4+4K_2SO_4$$

(equations *iii* and *iv* combined).
Here again, the evidence of the existence of oxidation-reduction potential for the reaction:

$$Mn^{3+}+FeCy_6^{4-} = Mn^{4+}+FeCy^{3-}$$

is forthcoming. The large value of

$$K = \frac{Mn^{4+}\times FeCy_6^{3-}}{Mn^{3+}\times FeCy_6^{4-}} = 3.09\times 10^7$$

point towards the possibility of Mn(III) being reduced to Mn(II) and the ferrocyanide oxidised to the ferricyanide during the course of the reaction (in fact, the reaction for the formation of manganic ferrocyanide would be a much slower process than the formation of ferric ferrocyanide). The amperometric titrations, however, failed to supply any information reagarding the formation of the complex $2KMn^{II}Fe^{III}Cy_6$ since the potential applied for these titrations could give an idea of the reaction taking place with Mn(III) only.

Reverse titrations give the ratio Mn^{3+} to $FeCy_6^{4-}$ as 2:1. The combining ratio does not fit any of the mentioned reactions. The probable reaction for this may be

$$K_4FeCy_6+2Mn_2(SO_4)_3=KMn^{III}\,Fe^{II}\,Cy_6+3K(MnSO_4)_2.$$

Although the reaction brings out indirectly one important fact, namely, the confirmation regarding the existence of the complex anion $Mn(SO_4)_2^-$ in the manganic solution (Ubbelhode, *loc. cit.*), it is rather difficult to visualise the possibility of such a reaction taking place in view of the oxidation potential existing in the system under investigation.

From the amperometric titrations between Mn(III) and potassium ferricyanide, the combining ratio comes out to be 1:1. Here again, the proof for the presence of the complex anion $Mn(SO_4)_2^-$ is forthcoming since the only possibility of the formation of the insoluble complex can be according to the reaction:

$$K_3FeCy_6+Mn_2(SO_4)_3=Mn^{III}\,Fe^{III}\,Cy_6+K_2SO_4+KMn(SO_4)_2.$$

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Studies on some Less Familiar Ferrocyanogen Complexes. Part VII. Composition of Cobalt (III) Ferro- and Ferricyanides by Electrometric Methods

M. Ajmal and Wahid U. Malik

Direct and reverse titrations between cobaltic sulphate and potassium ferrocyanide, and cobaltic sulphate and potassium ferricyanide have been carried out by conductometric, potentiometric, and amperometric methods. The cobaltic sulphate and potassium ferrocyanide reaction in view of high reduction potential of Co(III)—Co(II) system is expected to provide a complex of the type $Co_2^{II}Fe^{II}Cy_6$. Evidence for this complex has been obtained on the basis of these titrations. Besides a complex having the composition $Co^{III}Fe^{III}Cy_6$ is also found to exist. From the cobalt (III)-potassium ferricyanide reaction, adsorption complexes of the type $2Co^{III}Fe^{III}Cy_6.K_3FeCy_6$ and $2Co^{III}Fe^{III}Cy_6.3\,K_3FeCy_6$ are obtained besides the normal complex $Co^{III}Fe^{III}Cy_6$. The nature of the reverse amperometric titration curves also supports the formation of adsorption complexes in cobaltic ferricyanide.

Amongst the metal ferrocyanogen complexes, cobalt (III) compounds have attracted little attention by the workers in this field. The only reference worth mentioning is on the spectrophotometric estimation of Fe(II), ferrocyanide, and cerium (III) by cobalt (III) sulphate solution (Bricker and Loeffler, *Anal. Chem.*, 1955, **27**, 1419).

On adding cobalt (III) sulphate solution to potassium ferrocyanide, a dark grey precipitate is obtained, which changes to a brown one with excess of cobalt (III). Potassium ferricyanide also reacts with cobalt (III) to give a precipitate with the only difference that the initial colour of the precipitate (brown) does not change on further addition of cobalt (III). Since no work was done till recently on the composition of these freshly precipitated complexes, it was thought worthwhile to take up these studies specially in view of the fact that the interaction between cobalt (III) and potassium ferrocyanide would not be a simple one on account of the high reduction potential of cobalt (III)—cobalt (II) couple (1.82V vs. standard hydrogen electrode).

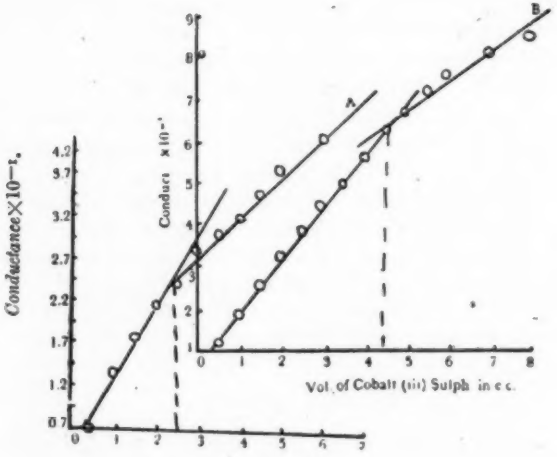
EXPERIMENTAL

The cobaltic sulphate solution was prepared by the modified method of Bricker and Loeffler (*loc. cit.*). The solution (with crystals in the bottom) obtained was stored in a 250c.c. glass stoppered flask and kept in a refrigerator at about 0°. The stock solution was diluted with cold 18*N*-H_2SO_4 prior to use. The strength of the solution was first determined iodometrically. Here the end point was not sharp and therefore the method recommended by Rausch and Kleinberg (T. Moeller, "Inorganic Synthesis", Vol. V, p. 183) was employed. One c.c. of the cobaltic solution was added to 10 c.c. of 0.1*N* oxalic acid solution. This solution was diluted to 100 c.c. and the unoxidised acid was then titrated by potassium permanganate solution, which was standardised against oxalic acid. The strength was found to be 0.059*M* and was checked occasionally. The strength did not change even on keeping the solution (in refrigerator) for longer periods.

Potassium ferrocyanide (A.R.) and potassium ferricyanide (recrystallised) were dissolved in double distilled water . The strengths of the solutions were determined volumetrically by titrating against potassium permangante and sodium thiosulphate respectively (Sutton, "Volumetric Analysis", 10th ed., pp. 270, 220).

The conductivity measurements were carried out by a Cambridge conductivity bridge No. L. 350140 with cell of $k=0.36$, whereas the potentiometric studies were carried out with a Tinsley vernier potentiometer employing bright platinum as the indicator electrode. For the amperometric titrations, the same procedure was employed as given in Parts V and VI (this issue, pp. 297,303) Before carrying out the titrations, a polarogram was taken by introducing 5 c.c. of cobalt(III) sulphate solution in $18N$-H_2SO_4 with 0.05% gelatin in the polarographic cell. A layer of CCl_4 was put below the solution in order to minimise the possible oxidation of mercury by Co^{3+}. Purified nitrogen gas was passed for deaeration and creating an inert atmosphere. The current remained constant in the initial stages, showing a little increase, giving an ill-defined wave, followed by a well-defined reversible wave due to the reduction of cobalt (II) to the metallic state. The titrations were carried out at 0.0 volt and also at 0.8 volt (from the plateau of the first wave). No difference, however, was found by carrying out the titrations at either of these potentials.

The conductance, E.M.F., and current measurements were carried out at 0°. While carrying out the direct titrations [cobalt (III) solution in the burette] the cobaltic sulphate solution was taken in a flask placed in a freezing mixture and pumping the solution into the microburette from it.



Volume of cobalt (III) *sulph. in c.c.*

FIG. 1. Conductometric titration curves.

A. 30 c.c. of 0.00 5M-K_4FeCy_6 against 0.059 Co (III) sulphate.
B. 30 c.c. of 0.02M-K_3FeCy_6 against 0.044 M Co (III) sulphalte.

Typical curves for the three techniques employed are shown in Figs. 1, 2, and 3 and the results are summarised below. Reverse conductometric titrations could not be performed since the conductance of the cobaltic solution was so high that the addition of potassium ferro- or ferricyanide did not cause an appreciable change in the conductance.

TABLE I

Titrations carried out between Co(III) *and* K_4FeCy_6.

Conc. of K_4FeCy_6.	Conc. of Co (III).	Ratio at the inflection point.
	(I) Conductometric.	Co^{3+} : $FeCy_6^{4-}$.
0.0100*M*	0.059*M*	1:1
0.0066	0.059	1:1
0.0050	0.059	1:1
Direct.	(II) Potentiometric.	
0.02	0.059	1:1
0.01	0.059	1:1
0.005	0.059	1:1
Reverse.		
0.2	0.044	1:1, 1:3
0.2	0.026	1:1, 1:3
0.2	0.020	1:1, 1:3
Direct.	(III) Amperometric.	
0.010	0.0285	1:1
0.005	0.0285	1:1
0.007	0.0285	1:1
Reverse.		
0.2	0.007	1:1
0.2	0.011	1:1
0.2	0.014	1:1

TABLE II

Titrations carried out between Co(III) *and* K_3FeCy_6.

Conc. of K_3FeCy_6.	Conc. of Co (III). Conductometric.	Ratio at the inflexion point. Co^{3+} : $FeCy_6^{3-}$.
0.020*M*	0.044*M*	1:3
0.010	0.044	1:3
0.0066	0.044	1:3
Direct.	Potentiometric.	
0.0180	0.037	1:3
0.0110	0.059	1:3
0.0092	0.059	1:3
Reverse.		
0.2	0.026	1:2, 1:5
0.2	0.025	1:2, 1:5
0.2	0.020	1:2, 1:5
0.2	0.010	1:2, 1:5
Direct.	Amperometric.	
0.020	0.034	1:3
0.015	0.034	1:3
0.010	0.034	1:3
Reverse.		
0.2	0.0080	1:2, 1:5
0.2	0.0069	1:2, 1:5
0.2	0.0051	1:2, 1:5

DISCUSSION

The combining ratio $Co^{3+} : FeCy_6^{4-}$ as 1:1, obtained from the direct potentiometric and conductometric titrations and also from direct and reverse amperometric titrations, would normally point towards the formation of the complex $KCo^{III}Fe^{II}Cy_6$. Such a reaction, however, is not possible in view of the high reduction potential of Co (III)—Co(II) system. For the reaction:

$$Co^{3+} + FeCy_6^{4-} \rightleftharpoons Co^{2+} + FeCy_6^{3-}$$

the value of K, calculated from the values -0.356 (for $FeCy_6^{4-} = FeCy_6^{3-} + e$) and -1.82 (for $Co^{3+} + e = Co^{2+}$), is 6.3×10^{25}. The high value of K indicates that the potassium ferrocyanide would be oxidised to the ferricyanide, whereas the cobalt (III) is reduced to cobalt (II). Under these conditions the reaction between cobaltic sulphate and potassium ferrocyanide can take either of the following courses:

$$Co_2(SO_4)_3 + 2K_4FeCy_6 \longrightarrow 2CoSO_4 + 2K_3FeCy_6 + K_2SO_4$$

followed by

(*i*) $2CoSO_4 + K_4FeCy_6 \longrightarrow Co_2^{II}Fe^{II}Cy_6 + 2K_2SO_4$, or

(*ii*) $CoSO_4 + K_3FeCy_6 \longrightarrow KCo^{II}Fe^{III}Cy_6 + K_2SO_4$, or

(*iii*) $Co_2(SO_4)_3 + 2K_3FeCy_6 \longrightarrow 2Co^{III}Fe^{III}Cy_6 + 3K_2SO_4$

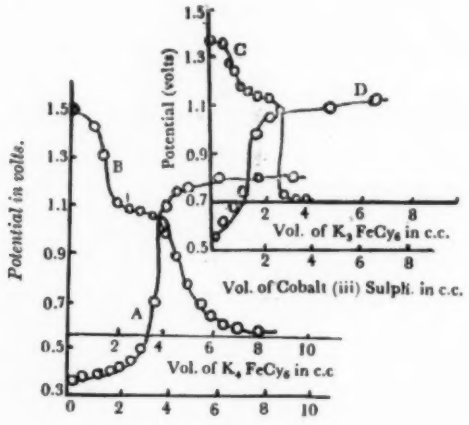


FIG. 2. Potentiometric titration curves.

Direct. A. 10 c.c. of 0.02 *M*-K_4 FeCy6 against 0.059 *M*-Co (III) sulphate.
Reverse. B. 10 c.c. of 0.025 *M*-Co (III) sulphate against 0.2 *M*-K_4 FeCy6.
Reverse. C. 10 c.c. of 0.01 *M*-Co (III) sulphate against 0.2 *M*-K_3 FeCy6.
Direct. D. 10 c.c. of 0.018 *M*-K_3 FeCy6 against 0.037 *M*-MCo (III) sulphate.

The formation of the above three complexes would depend not only on the presence of excess of either of the reactants in the reaction mixture but also on their affinity for each other. For example, Bricker and Loeffler (*loc. cit.*) reported the existence of the complex $Co_3(Fe^{III}Cy_6)_2$ by the interaction of cobalt (III) and potassium ferrocyanide even when

potassium ferrocyanide was in excess. As regards the stoichiometric equations representing the overall reaction for the possible complexes for the cobalt (III)—potassium ferrocyanide reaction, we have:

$$(a)\quad Co_2(SO_4)_3 + 3K_4FeCy_6 \rightarrow Co_2^{II}Fe^{II}\,Cy_6 + 2K_3FeCy_6 + 3K_2SO_4$$

$$(b)\quad Co_2(SO_4)_3 + 2K_4FeCy_6 \rightarrow KCo^{II}Fe^{III}Cy_6 + 3K_2SO_4$$

$$(c)\quad Co_2(SO_4)_3 + K_4FeCy_6 \rightarrow Co^{III}Fe^{III}Cy_6 + 2K_2SO_4 + CoSO_4$$

Since the ratio 1:1 forthe reactants is obtained at the inflection points from the direct potentiometric and conductometric titrations as well as from the direct and reverse amperometric titrations, the complex formed would be $Co^{III}Fe^{III}Cy_6$ according to the equation (*c*). Proof for the formation of cobaltous ferrocyanide, predominance of which should always be expected on the redox nature of the reaction, is also forthcoming on the basis of the reverse potentiometric titrations. It may thus be concluded that besides the formation of cobaltous ferrocyanide, cobaltic ferricyanide complex is also likely to be formed during the interaction of cobaltic sulphate and potassium ferrocyanide.

On adding cobalt(III) sulphate solution to potassium ferricyanide, the combining ratio $Co^{3+} : FeCy_6^{3-}$ comes out to be 1:3 (direct conductometric, potentiometric, and amperometric titrations, Figs. 1. 2, and 3) whereas for the reverse order of mixing, the ratios are 1:2 and 1:5 (reverse potentiometric and amperometric titrations; Figs. 2 and 3).

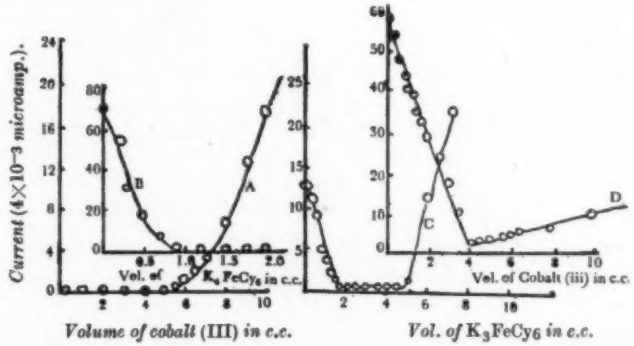


FIG. 3. Amperometric titration curves.

Direct. A. 20 c.c. of 0.01 *M*-K_4 FeCy6 against 0.028 *M*-Co (III) sulphate.
D. 20 c.c. of 0.02 *M*-K_3FeCy6 against 0.034 *M*-Co (III) sulphate.
Reverse. B. 20 c.c. of 0.007 *M*-Co (III) sulphate against 0.2 *M*-K_4 FeCy6.
C. 20 c.c. of 0.008 *M*-Co (III) sulphate against 0.2 *M*-K_3 FeCy6.

The ratio 1:2 would point towards the formation of the complex $Co^{III}Fe^{III}Cy_6$ according to the equation:

$$Co_2(SO_4)_3 + 2K_3FeCy_6 = 2\ Co^{III}Fe^{III}Cy_6 + 3K_2SO_4$$

The ratios 1:3 and 1:5 would obviously form adsorption complexes having the composition $2CoFeCy_6.K_3FeCy_6$ and $2CoFeCy_6.\ 3K_3FeCy_6$ respectively.

The existence of the adsorption complexes can also be inferred from the reverse amperometric titration curves (Fig. 3). On adding potassium ferricyanide to cobaltic sulphate solution, the current goes on decreasing after which it remains constant for a wide

range of the added titrant and then increases. The horizontal part of the curve might represent conditions where the freshly precipitated cobaltic ferricyanide complex strongly adsorbs the ferricyanide ions.

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Diphenylcarbazide and Diphenylcarbazone. Part II. Polarographic Study on Diphenylcarbazone

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A polarographic study of the system $RH_2+2H^++2e^- \rightleftharpoons RH_4$, has been made ($RH_2$=diphenylcarbazone and RH_4=diphenylcarbazide). The reaction appears to be an irreversible one at the dropping mercury cathode. $E_{\frac{1}{2}}$ values found against S.C.E. and mercury pool anode are +0.085V and −0.042V respectively at 32°. The polarographic estimation of diphenylcarbazone at pH=0.7 has been described. The interference due to diphenylcarbazide has also been studied. The polarograms for the coloured solutions, formed by the reaction between chromic acid and diphenylcarbazide in different ratios, indicate the presence of free diphenylcarbazone as one of the reaction products and another reducible compound, presumably to be a complex compound of chromium with diphenylcarbazone.

In our previous communication (this *Journal*, 1960, **37**, 650), the volumetric estimation of diphenylcarbazide and diphenylcarbazone has been described. The present paper constitutes a study on diphenylcarbazone polarographically. It has been assumed that diphenylcarbazone is reduced at the dropping mercury cathode according to the equation:

$$RH_2+2H^++2e^- \rightleftharpoons RH_4 \qquad .. \qquad .. \qquad (1)$$

where RH_2=diphenylcarbazone and RH_4=diphenlycarbazide. It is apparent that $E_{\frac{1}{2}}$ values of the system are dependent on hydrogen-ion concentration. The effect of pH on $E_{\frac{1}{2}}$ values has been studied systematically and the values are found to be fairly constant at pH ranges between 1.3 and 0.6. So the polarographic estimation has been undertaken at these pH ranges.

The reaction (1) appears to be irreversible, as the straight line could not be drawn through all the points by plotting $E_{d.e.}$ versus log $(i_d-i)/i$. The interference due to diphenylcarbazide in the estimation of diphenylcarbazone has been studied and the results are found to follow an empirical relation:

$$E'_{\frac{1}{2}} = E_{\frac{1}{2}}+0.03 \log \left(1+\frac{2RH_4}{RH_2}\right) \qquad .. \qquad .. \qquad (2)$$

where $E_{\frac{1}{2}}$=half-wave potential and $E'_{\frac{1}{2}}$=observed half-wave potential. The $E'_{\frac{1}{2}}$ values are found to be shifted towards less negative, which may be due to slower reaction rates of this conjugate oxidant-reductant pair.

Polarograms, obtained for the coloured solutions formed by the reaction between chromic acid and diphenylcarbazide in different ratios, indicate the presence of free diphenylcarbazone as one of the reaction products and another reducible compound, which is pro-

bably the complex compound of chromium with diphenylcarbazone. As it has already been shown by Job's method of continued variation (Bose, *Anal. Chim. Acta*, 1954, **10**, 209; Pflaum and Howick, *J. Amer. Chem. Soc.*, 1956, **78**, 4862) that maximum coloration takes place while reacting at the ratio of two moles of chromic acid to three moles of diphenylcarbazide, the reaction may therefore be represented in the following way:

$$2HCrO_4^- + 3RH_4 + 8H^+ \rightleftharpoons 2CrRH_2^{3+} + RH_2 + 8H_2O.$$

Further investigations are in progress.

EXPERIMENTAL

Polarographic measurements were carried out on a Cambridge pen recording polarograph and against the mercury pool anode except otherwise mentioned. The electrode employed has a drop time of 3.15 sec. and a mass-drop time ($m^{\frac{2}{3}} t^{\frac{1}{6}}$) value of 1.59 (in water at zero-volt applied potential).

Diphenylcarbazone was purified by recrystallisation from ether. Glacial acetic was distilled over chromic acid. Other reagents employed were of A.R. quality.

A known amount of diphenylcarbazone (appr. 0.012 g.) was dissolved in glacial acetic acid (12.5 c.c.) and diluted to 50 c.c. with water; an aliquot was used for polarographic study. The solutions electrolysed were composed of known volumes of diphenylcarbazone solution, (the supporting electrolyte potassium nitrate), and water to dilute to a required volume; *p*H of the solutions was varied from 4.98 to 0.56 by adding either dilute sulphuric acid or sodium hydroxide solution, whichever was necessary. The solutions were deoxygenated by bubbling hydrogen for 15 minutes and polarograms were obtained over the range 0.05V to-0.15V. The results are recorded in Table I.

TABLE I

Diphenylcarbazone (0.0244 g.) was dissolved in 25 c.c. of acetic acid and diluted with water to 100 c.c. An aliquot of 5 c.c. was taken for each subsequent solution. The final volume was made to 25 c.c. with water. Sensitivity=1/5. Damping=3.

2*M*-KNO_3.	1.64*N*-KOH.	1*N*-H_2SO_4.	3.63*N*-AcOH.	*p*H.	$E_{\frac{1}{4}}$.
6.1 c.c.	7.70 c.c.	..	..	4.98	-0.054 volts
8.8	4.40	..	..	4.48	-0.048
10.7	2.20	..	..	4.04	-0.046
11.2	1.65	..	..	3.82	-0.045
12.0	0.55	..	..	3.31	-0.045
12.3	0.20	..	..	2.75	-0.044
12.5	..	..	..	2.17	-0.044
12.5	..	..	5.0	2.08	-0.044
12.5	..	0.50 c.c.	..	1.65	-0.043
12.5	..	1.00	..	1.32	-0.042
12.5	..	2.50	..	0.98	-0.042
12.5	..	5.00	..	0.70	-0.042
12.5	..	7.00	..	0.56	-0.042

Typical polarograms are shown in Fig. 1. $E_{\frac{1}{2}}$ values were found to be +0.085V and −0.042V at 32° against S.C.E. and mercury pool anode respectively.

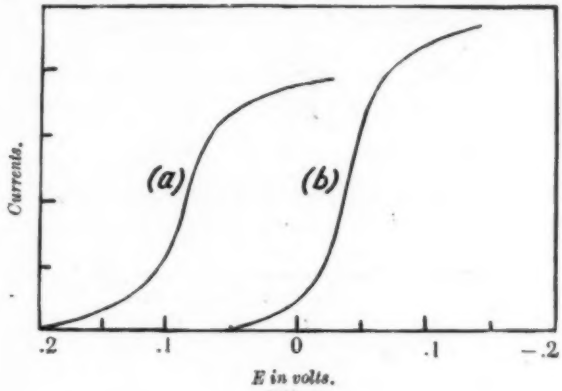

FIG. 1

(*a*) Against S.C.E. Sensitivity = 1/15. Damping = 3. $C_{RH_2} = 4.3 \times 10^{-4}$ *M*.
(*b*) ,, mercury pool anode. Sensitivity = 1/5. Damping = 3. $C_{RH_2} = 2.0 \times 10^{-4}$ *M*.

Polarographic estimation of diphenylcarbazone was carried out at *p*H 0.7. The results obtained are recorded in Table II.

TABLE II

Diphenylcarbazone (0.0120 g.) was dissolved in 12.5 c.c. of acetic acid and diluted to 50 c.c. with water. Different volumes of this solution, 10 c.c. of 2*M*-KNO_3 and 5 c.c. of 1*N*-H_2SO_4 were taken and diluted to 25 c.c. with water. Sensitivity = 1/7. Damping = 3.

RH_2 solution.	Wave-height found.	Height per c.c.
6 c.c.	30.4	5.07
5	25.5	5.10
4	20.0	5.00

The interference due to diphenylcarbazide was studied. $E_{\frac{1}{2}}$ values were found to be shifted and consequently diphenylcarbazone could not be estimated polarographically in presence of diphenylcarbazide. The results were, however, found to follow the relation:

$$E'_{\frac{1}{2}} = E_{\frac{1}{2}} + 0.03 \log\left(1 + \frac{2RH_4}{RH_2}\right)$$

The results are shown in Table III.

TABLE III

Diphenylcarbazone (0.0122 g.) was dissolved in 12.5 c.c. of acetic acid and diluted to 50 c.c. with water (solution 'A'). The solution 'B' was of diphenylcarbazide (0.0125 g.) in 12.5 c.c. of acetic acid and the volume was made to 50 c.c. with water. For each subsequent solution 5 c.c. of 'A', 10 c.c. of 2*M*-KNO_3, 5 c.c. of 1*N*-H_2SO_4 and, different volumes of 'B' were taken and diluted to 25 c.c. with water.

TABLE III (contd.)

Solution 'B'.	$E_{\frac{1}{2}}$ found.	RH_4/RH_2	
0.0 c.c.	-0.042 volts	Found.	Calc.
0.2	-0.041	0.040	0.041
0.6	-0.039	0.130	0.123
1.0	-0.037	0.234	0.203
2.0	-0.034	0.424	0.406
3.0	-0.032	0.577	0.609
5.0	-0.028	0.965	1.016

Polarograms were obtained of the coloured solutions prepared by mixing diphenylcarbazide and chromic acid in different ratios in presence of $0.2N$-H_2SO_4 and $0.8M$-KNO_3. These are shown in Fig. 2.

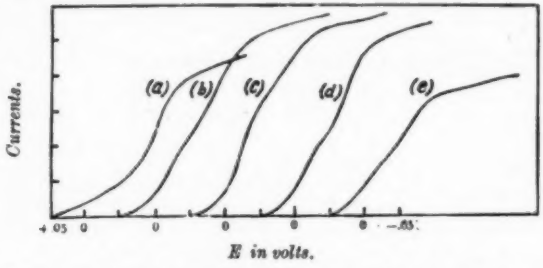

FIG. 2. Ratio of chromic acid to diphenylcarbazide. (*a*) 1.10, (*b*) 0.85. (*c*) 0.66. (*d*) 0.60. (*e*) 0.50.

Examination of the polarographic waves indicates that the first step is due to diphenylcarbazone, $E_{\frac{1}{2}}$ values appearing to be shifted toward less negative where ratios <0.67 are evidently due to the presence of unchanged diphenylcarbazide. $E_{\frac{1}{2}}$ values of the second step are shifted toward more negative, due perhaps to complex-bound diphenylcarbazone.

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Separation and Identification of Micro-quantities of Metallic Ions by Ring Oven Technique using Tartrate as a Complexant

Eric John Singh and Arun K. Dey

A simple microanalytical method for separation of metallic ions of the same group of qualitative analysis [Hg(I), Pb(II), Ag(I), Hg(II), Bi(III), Cu(II), Cd(II), As(III), Sb(III), and Sn(II)] with tartrate as complexing agent, using ring oven technique, has been studied. With the addition of the complexing agent, the separations improve with distinct separation zones, whereas in the absence of the same, no distinct separation is possible. The complete separation and identification of a group of elements can be made within five minutes.

It is well known that complex formation plays an important role in the separation of ions in filter paper chromatography, as pointed out by us in a previous paper (Singh and Dey, this *Journal*, 1961, **38**, 193). We have also observed the variation in the migration of ions on filter paper strips in presence of tartrate as a complexant (*Z. anal. Chem.*, 1959, **165**, 81). Following the ring oven technique outlined by Weisz (*Microchim. Acta*, 1954, **140**, 367, 787), we separated metal ions, with oxalate, citrate, and EDTA as complexants (unpublished. In this paper the separation of metallic ions of the same group, using tartrate as the complexant by the same technique, has been described.

EXPERIMENTAL

Weisz ring oven, manufactured by National Appliance Co., U.S.A., was used. The heating was done by connecting the leads of the apparatus through a dimmerstat (Automatic Electrical Devices, Bombay) giving 25 volts from 220 volts/50 cycles A.C. mains. The temperature of the heating block was 100°.

Procedure.—Standard solutions of nitrates of Pb(II), Hg(I), Ag(I), Cu (II), Hg(II), Cd(II), Bi(III), Co(III) and chlorides of Sb(III), Sn(II), As(III), and sodium tartrate (reagent grade chemicals) were prepared. Whatman filter No. 1 was used. 60% Ethanol was used as solvent. Ternary, quaternary, and pentanary mixtures, generally of the same group, containing equal concentrations of the metal solutions with varying proportions of sodium tartrate were prepared, keeping the total volume constant. The ratio of the total concentration of the metals (obtained by adding the concentrations in molarity of the metals) to the concentration of tartrate added, has been expressed as the metal tartrate ratio (equivalents of tartrate). A very small drop of the ternary, quaternary, and pentanary mixtures having a volume of 0.0035c.c. was taken in a micropipette and dropped at the centre of the paper. This paper was placed on the cylindrical block and kept stationary with the help of the aluminium ring and dried by heating. The spot was treated three times by dropping the solvent through the capillary pipette, inserted into the guide tube of the ring oven. The chromatograms were dried on the ring oven and developed by means of suitable indicators. The sequence of ions mentioned in the following description refers to the position of the rings from the centre to the outer edge, as a result of separation.

In ternary, quaternary, and pentanary mixtures, the final concentrations of each of the metal ions were 0.033*M*, 0.025*M*, and 0.02*M* respectively.

Separation of Ag(I), Hg(I) *and* Pb(II).—The separation of these metal ions is possible up to the addition of 0.48 equivalents of the complexing agent. With higher concentrations of the same, no separation is possible. A good separation was obtained when 0.16 to 0.3

equivalents of the complexing agent were used. The sequence of separation is Hg(I)-Ag(I)-Pb(II). The chromatograms were marked when these were moist. A complete separation and identification of the first group elements can be made in four minutes.

Separation of Cu(II), Cd(II), *and* Hg(II).—No separation is possible without the addition of the complexing agent. The separation of Cu(II), Cd(II), and Hg(II) ions is obtained when 1 to 1.6 equivalents of the complexing agent are used. Beyond 1.6 equivalents of the same, separation is not possible due to spreading and overlapping of the zones. The sequence of separation is Cd(II)-Hg(II)-Cu(II).

Separation of Cu(II), Cd(II), *and* Bi(III).—In the separation of these ions, only Bi(III) ions could be separated by addition of tartrate as a complexing agent. The sequence of separation is Bi(III)-[(Cu(II)-Cd(II)].

Separation of Cu(II), Cd(II), *and* Pb(II).— Only the separation of lead (II) is possible up to the addition of 0.80 equivalent of tartrate. It may be seen that a feeble separation is obtained when 1.0 to 1.6 equivalents of the complexing agent are used. The sequence of separation is Pb (II)-[Cu(II)-Cd (II)]. This separation is not sharp due to spreading of copper (II) and cadmium (II) zones.

Separation of Cu(II), Cd(II), Pb(II), *and* Hg(II).—No sharp separation of the metallic ions is possible under the experimental conditions due to the spreading of the zones. The sequence of separation, however, is found to be [Pb(II)-Hg(II)]-Cd(II)-Cu(II) up to the addition of 0.36 equivalents of tartrate and with higher concentration of the same, no separation occurs. With the addition of 0.48 or more equivalents of the complexing agent, most of the Cu(II) ions do not move from the initial spot.

Separation of Cu(II), Cd(II), Hg(II), Pb(II), *and* Co(II).—No satisfactory separation of ions is possible with tartrate as complexing agent due to spreading and overlapping of zones.

Separation of As(III), Sb(III), *and* Sn(II).—The separation was effected up to the addition of 0.96 equivalents of tartrate. With higher concentration of the same, the separation was not possible. The sequence of separation is Sb(III)-As(III)-Sn(II). The complete separation and identification of second B group elements can be made in four minutes.

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Reactive Methylene Compounds. Part VIII. Condensations with Benzenediazonium Salts

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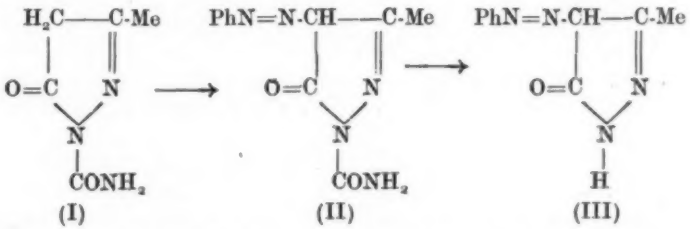
Benzenediazonium salts have been condensed with diethyl malonate, 1-carbamoyl-3-methyl-5-pyrazolone, indan-1,3,-dione, and methone. Characteristics of the products obtained have been described.

The work on the condensation of reactive methylene compounds with benzenediazonium salts has been extended (Garg and Joshi, this *Journal*, 1960, **37**, 626; Garg, *ibid.*, 1961, **38**, 113, 115); the coupling of diethyl malonate, 1-carbamoyl-3-methyl-5-pyrazolone, indan-1,3-dione, and methone with some phenyldiazonium salts has been described in this paper.



It has been observed that 1-carbamoyl-3-methyl-4-(substituted benzeneazo)-5-pyrazolones (II) loose carbamoyl group, when heated in alcohol, forming 3-methyl-4-(substituted benzeneazo)-5-pyrazolones(III).

EXPERIMENTAL**

Diethyl malonate was commercially available. 1-Carbamoyl-3-methyl-5-pyrazolone was prepared by cyclization of semicarbazone of ethyl acetoacetate in presence of ammonia. The latter was obtained from ethyl acetoacetate and semicarbazide. Indan-1,3-dione (Teeters and Shriner, *J. Amer. Chem. Soc.*, 1933, **55**, 3027) and methone (Vorländer, *Z. anal. Chem.*, 1929, **77**, 245) were prepared by known methods.

Condensation of Benzenediazonium Salts with Reactive Methylene Compounds.—The benzenediazonium salts were condensed with diethyl malonate, 1-carbamoyl-3-methyl-5-pyrazolone, indan-1,3-dione, and methone in the same manner, as described in earlier communications (Garg and Joshi, *loc. cit.*). Characteristics of the various compounds obtained are reported in Tables I and II.

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** Melting points are uncorrected.

TABLE I

No.	Benzeneazo derivative formed.	Diethyl malonate %Yield.	M.P.	Colour,	Formula.	Found.	Calc.	1-Carbamoyl-3-methyl-5-pyrazolone. %Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1.	4-Methoxy-	-	-	-	-	-	-	86	201°	Red	$C_{12}H_{13}O_3N_5$	N:25.68%	25.45%
2.	2-Chloro-	79	73°	Pale yellow	$C_{13}H_{15}O_4N_2Cl$	Cl: 11.69%	11.89%	91	210°	Yellow	$C_{11}H_{10}O_2N_5Cl$	Cl:12.38	12.70
3.	3-Chloro-	-	-	-	-	-	-	92	203°	Do	$C_{11}H_{10}O_2N_5Cl$	Cl:12.29	12.70
4.	4-Chloro-	-	-	-	-	-	-	93	205°	Do	$C_{11}H_{10}O_2N_5Cl$	Cl:12.41	12.70
5.	4-Nitro-	83	78°	Pale yellow	$C_{13}H_{15}O_6N_3$	N: 13.31	13.59	94	266°	Golden yellow	$C_{11}H_{10}O_4N_6$	N:28.68	28.96
6.	3-Nitro-	79	88°	Yellow	$C_{13}H_{15}O_6N_3$	N: 13.28	13.59	92	211°	Yellow	$C_{11}H_{10}O_4N_6$	N:28.71	28.96
7.	4-Methyl-	78	71°	Do	$C_{14}H_{18}O_4N_2$	N: 9.92	10.07	86	192°	Do	$C_{12}H_{13}O_2N_5$	N:26.88	27.02
8.	2-Chloro-4-nitro-	79	95°	Chocolate	$C_{13}H_{14}O_6N_3Cl$	Cl: 10.12	10.33	92	201°	Dark brown	$C_{11}H_9O_4N_6Cl$	Cl:10.71	10.93
9.	2-Nitro-4-chloro-	81	98°	Red	$C_{13}H_{14}O_6N_3Cl$	Cl: 10.01	10.33	90	244°	Yellow	$C_{11}H_9O_4N_6Cl$	Cl:10.83	10.93

TABLE II

No.	Indan-1,3-dione. %Yield.	M.P.	Colour.	Formula.	Found.	Calc.	Methone. %Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1.	88	179°	Orange-red	$C_{16}H_{12}O_3N_2$	N : 9.97%	10.00%	-	-	-	-	-	-
2.	92	234°	Dirty yellow	$C_{15}H_9O_2N_2Cl$	Cl : 12.41	12.47	92	124°	Golden yellow	$C_{14}H_{15}O_2N_2Cl$	Cl:12.48%	12.75%
3.	92	178°	Do	$C_{15}H_9O_2N_2Cl$	Cl : 12.27	12.47	93	122°	Light orange	$C_{14}H_{15}O_2N_2Cl$	Cl:12.51	12.75
4.	92	235°	Violet	$C_{15}H_9O_2N_2Cl$	Cl : 12.41	12.47	93	210°	Pale yellow	$C_{14}H_{15}O_2N_2Cl$	Cl:12.61	12.75
5.	95	280°	Yellow	$C_{15}H_9O_4N_3$	N : 14.02	14.23	96	216°	Yellow	$C_{14}H_{15}O_4N_3$	N:14.53	14.53
6.	93	296°	Brownish yellow	$C_{15}H_9O_4N_8$	N : 13.98	14.2g	-	-	-	-	-	-
7.	-	-	-	-	-	-	-	-	-	-	-	-
8.	92	238°	Dirty yellow	$C_{15}H_8O_4N_3Cl$	Cl : 0.61	10.77	93	178°	Brown	$C_{14}H_{14}O_4N_3Cl$	Cl:10.68	10.9
9.	92	239°	Red	$C_{15}H_8O_4N_3Cl$	Cl : 10.58	10.77	93	165°	Brown	$C_{14}H_{14}O_4N_3Cl$	Cl:10.72	10.97

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Oxine *N*-Oxide as an Analytical Reagent for the Colorimetric Estimation of Cerium (IV) and its Comparison with Oxine as a Chelating Agent

A. N. Bhat and B. D. Jain

Oxine *N*-oxide has been investigated as an analytical reagent for the colorimetric estimation of cerium (IV), which produces a deep brownish red, water-soluble complex with an ethanolic solution of the reagent. The complex is quite stable and the intensity of the colour remains unchanged between *p*H 2.0 and 6.5. The complex obeys Lambert-Beer's law at 420 mμ up to a dilution of 9 p.p.m. of cerium. The trivalent rare earths cerium, lanthanum and yttrium do not interfere in the above estimation.

Very little is known about the formation of co-ordination compounds with heterocyclic *N*-oxides ((Katritzky, *Quart. Rev.*, 1956, **10**, 395). *N*-Oxides form stable salts with strong acids unless other negative groups are present. The basicity is, however, considerably less than that of the corresponding parent compound; the *pK* values of the conjugate acids of (e.g.) pyridine and pyridine *N*-oxide are respectively 5.29 and 0.79 (Jaffe and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441). We carried out the study of oxine *N*-oxide as an analytical reagent and investigated in detail its uranium (VI) and iron (III) complexes spectrophotometrically (Bhat and Jain, *J. Sci. Ind. Res.*, 1960, **19 B**, 16, 295). The *pK* value of oxine *N*-oxide has now been determined by *p*H titrations in 50% (v/v) dioxane—water mixture and it is found to be 4.6 as compared to 10.8 for oxine (Irving and Rossotti, *J. Chem. Soc.*, 1954, 2910). The basicity of oxine *N*-oxide is thus considerably decreased by the introduction of the $N^+—O^-$ in the heterocyclic molecule, with the result that the metal chelates of oxine *N*-oxide become less stable than those of oxine (Bhat *et al.*, *loc. cit.*).

During our spectrophotometric studies of uranium (VI)-oxine *N*-oxide complex, it was observed that cerium (IV) ions seriously interfered in the estimation of uranium and this led us to study the reaction of cerium(IV) with oxine *N*-oxide. We have found that this reagent has certain advantages over oxine for the colorimetric determination of cerium(IV).

Although several organic reagents have been developed for their colorimetric reactions with cerium(IV), few have been adapted to quantitative colorimetric determination (Snell and Snell, "Colorimetric Methods of Analysis", Vol II, 1954, p. 607). Since tetravalent cerium ion is yellow, that furnishes one direct means of determination. Some of the organic reagents recommended for colorimetric determination of cerium are brucine (Shemyakin and Volkova, *J. Gen. Chem.*, 1939, **9**, 698), pyrogallol (Shemyakin *et al.*, *ibid.*, 1935, **5**, 667), and gallic acid (Shemyakin, *Zavodskaya Lab.*, 1934, **3**, 1090). These reagents suffer from various disadvantages. For instance, brucine lacks sensitivity and the intensity of the colour produced increases with time. In the case of pyrogallol, the colour formed varies from a violet sol to a dark purple-red precipitate, depending on the concentration of the reagents. Both pyrogallol and gallic acid can be used only at high *p*H. Tiron (Sarma, *J. Sci. Ind. Res.*, 1955, **14B**, 538), which gives water-soluble complex, has also been used. Westwood and Mayer (*Analyst*, 1948, **73**, 275) used oxine for the extraction in chloroform of cerous ions from aqueous solutions having *p*H 9.9-10.5.

When an ethanolic solution of oxine *N*-oxide is treated with an aqueous solution of cerium (IV) salt, a deep brownish red, water-soluble complex is instantaneously produced. The complex is quite stable and the colour remains unchanged between *p*H 2.0 and 6.5. The complex obeys Lambert-Beer's law to a dilution of 9.0 p.p.m. of cerium and the optical density remains unaffected between 10° and 30°. The reagent has an additional advantage, namely, no special organic solvent is needed for extraction of the complex since it is water-soluble. The trivalent rare earths cerium, lanthanum, and yttrium do not interfere.

EXPERIMENTAL

Oxine *N*-oxide was prepared by the method previously described (Bhat *et al.*, *loc. cit.*). Standard cerium (IV) solutions were prepared with cerium (IV) ammonium nitrate (B.D.H., A.R.). All other reagents were either of A.R. or *pro analysi* quality.

The absorption spectra studies of cerium (IV)-oxine N-oxide complex were made with a Unicam spectrophotometer SP 600. All other absorption measurements were made using a Lumetron photoelectric colorimeter. A Beckman *p*H meter, Model H 2, was used for *p*H measurements.

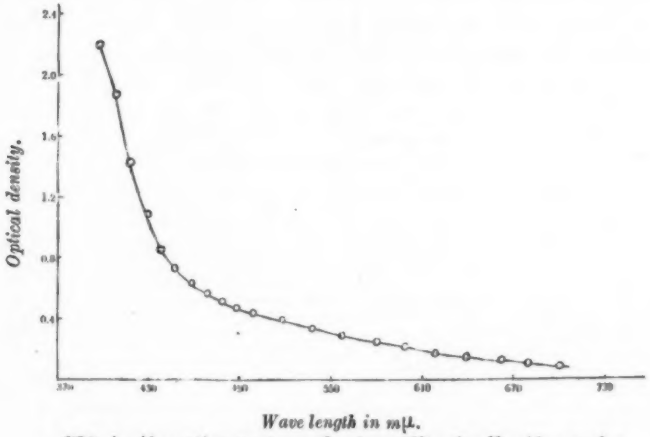


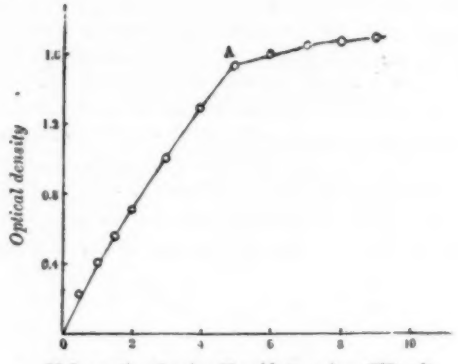
FIG. 1. Absorption spectrum of cerium (IV)-oxine *N*-oxide complex.

Absorption Spectra.—The ultraviolet absorption spectrum of oxine *N*-oxide has already been reported (*loc. cit.*). The cerium (IV)-oxine *N*-oxide complex did not have any maximum absorption band in the visible region of the spectrum. The nature of the absorption curve (Fig. 1) shows that the absorption maximum must be in the ultraviolet region. The wave length filter 420 mμ was chosen for the subsequent colorimetric studies of the complex. At this wave length, the absorption due to the reagent was negligible.

Minimum Amount of Oxine N-oxide necessary for the Estimation of Cerium (IV).—The optical densities at 420 mμ of a series of solutions containing oxine *N*-oxide and cerium (IV) in the molar ratio of 0.5: 1 to 9:1 were determined. The results plotted in Fig. 2 show that the portion of the curve up to A is almost a straight line up to the molar ratio of 5.0. For the estimation of cerium (IV), however, the molar ratio of oxine *N*-oxide to cerium (IV) was maintained at 10 in the subsequent studies.

*Effect of p*H *on Cerium-oxine N-oxide Complex.*—The stock solution of the complex was 1.0×10^{-3} *M* with respect to cerium. An aliquot (10 c.c.) of this solution was taken in a 25c.c. measuring flask and the volume made to 25 c.c. using dilute solutions of HCl and

NaOH for *p*H adjustments. The complex showed a minimum and unchanged transmission between a wide *p*H range of 2.0 and 6.5 (Table I). The solution developed slight turbidity above *p*H 6.5. The *p*H of each of the solutions was determined using a suitable glass electrode.



Molar ratio of oxine N-oxide to cerium (IV) salt.

FIG. 2. Variation in the optical density of the complex solution with change in molar ratio of oxine N-oxide and Ce (IV).

TABLE I

No.	*p*H.	%Transmission.	No.	*p*H.	%Transmission.
1.	1.0	77.0	5.	3.3	66.0
2.	1.5	73.0	6.	4.4	65.5
3.	2.0	66.3	7.	6.0	65.5
4.	2.5	66.0	8.	6.5	65.5

Stability of the Colour of the Complex.—The colour of the cerium (IV)-oxine *N*-oxide complex was found to be quite stable and no change in the transmission percentage could be observed even after one week. The absorption by the complex remains unaffected between 10° and 30°.

Lambert-Beer's Law.—Varying known volumes of a stock solution of the ceric complex (strength 1.0×10^{-3} *M* with respect to ceric ions) were taken in a 25 c.c. measuring flask and the volume was made to 25 c.c. using distilled water. Transmission percentage in each case was found with the colorimeter using filter 420 mμ (Table II).

TABLE II

No.	Conc. of Ce(IV) ions (moles per litre).	%Transmission.
1.	0.06×10^{-3}	88.0
2.	0.10×10^{-3}	86.0
3.	0.20×10^{-3}	78.5
4.	0.40×10^{-3}	67.5
5.	0.60×10^{-3}	54.0
6.	0.80×10^{-3}	42.0
7.	1.00×10^{-3}	32.0

When the above concentrations of cerium (IV) ions are plotted against the transmission percentage, a straight line is obtained; this shows that Lambert-Beer's law is obeyed by the coloured complex up to a dilution of 9 p.p.m. of cerium in the solution.

Interference due to Foreign Ions.—The stock solution of the complex was $1.0 \times 10^{-3} M$ with respect to cerium, having 10 as the mole ratio of the reagent to the metal ion. Known volumes of this solution were taken in a 25 c.c. measuring flask and mixed with a known amount of a solution of the foreign salt; the volume was made to 25 c.c. with water. The transmission percentage of this solution was determined within five minutes of mixing. The concentration of the foreign salt was progressively increased till the transmission changed by 2% of the theoretical values. It was found that a solution containing 0.087 mg. of ceric ion could be estimated for the metal in presence of 0.6.mg./c.c. of cerium (III); the solution containing 0.029 mg. of ceric ion could be estimated in presence of 0.674 mg./c.c. of lanthanum (III) and 0.72 mg./c.c. of yttrium (III). Uranium, thorium, and fluoride ions, however, interfere in the above estimation and therefore their separation by usual methods is necessary before estimation of cerium (IV) with this reagent.

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SHORT NOTES

Synthesis of 2′-Hydroxy-5′-nitro-3′, 4′-benzo-chalkone Derivatives

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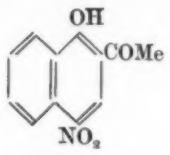
2-Hydroxy-3,4 benzo-5-nitroacetophenone was condensed with different aldehydes, viz., benzaldehyde, anisaldehyde, salicylaldehyde, and *m*-and *p*-hydroxybenzaldehydes with a view to studying the effect of the nitro group on the formation of chalkones and flavones. The condensation of these aldehydes with the ketone takes not less than 3 hours in presence of 40% NaOH. If sodium peroxide is used as a condensing agent, the aldehydes condense within 2 minutes to afford the chalkones. In the formation of chalkones sodium peroxide thus characterises itself in decreasing the reaction time to a minimum. The ease in which the condensation takes is in the order: *m*-hydroxy- > *p*-hydroxy- > *o*-hydroxy-aldehyde.



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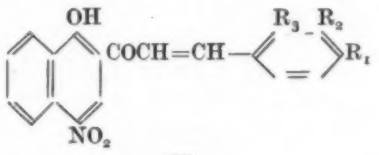

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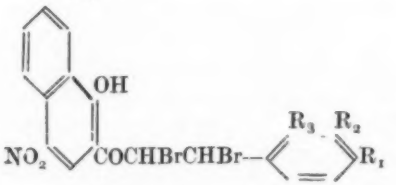

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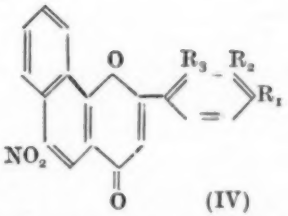

(IV)

2-Hydroxy-5-nitro-3,4-benzoacetophenone (I).— α-Naphthol acetate (14.4g.) was subjected to the Fries migration in presence of anhydrous aluminium chloride (20 g.) by keeping the mixture for 1 hour at 120° in an oil bath. The complex was decomposed with water and HCl (dil.) and the crude mass was crystallised from dilute acetic acid as white crystals (10.g.), m.p.96°. To 2-hydroxy-3,4-benzoacetophenone, dissolved in acetic acid (50 c.c.), HNO_3 (conc., 6 c.c.) was added dropwise with continuous stirring at a controlled temperature, not above 50°. Yellow needle-shaped crystals separated after 20 minutes, and stirring was continued for 15 another minutes. The crude mass after filtration at the pump was crystallised from acetic acid as straw-coloured needles (7g.), m.p. 162°. (Found: N, 5.8. Calc. N:6.0%). It dissoves in NaOH solution and develops a green colour with ethanolic ferric chloride.

Chalkones (II).—Ketone (I, 0.5 g.) and the corresponding aldehyde (1g.) were dissolved in ethanol (10 c.c.); 40% NaOH solution (2c.c.) was added to the boiling ethanolic solution. The solution was acidified after 3 hours and treated with boiling water to remove the

acid formed in the side reaction (sodium bicarbonate could not be used as it also dissolved the nitrochalkones) and the crude mass was crystallised from acetic acid; yield 0.25-0.3g. Only the chalkone of *p*-hydroxybenzaldehyde was crystallised from 50% acetic acid.

The following compounds have been prepared:

(*i*) $R_1=R_2=R_3=H$, m.p.208°.
(*ii*) $R_1=OMe$, $R_2=R_3=H$, m.p. 204°.
(*iii*) $R_3=OH$, $R_1=R_2=H$,m.p. 205°.
(*iv*) $R_2=OH$, $R_1=R_3=H$,m.p. 211°.
(*v*) $R_1=OH$, $R_2=R_3=H$, m.p. 158°.

Percentage of nitrogen is in accord with the value calculated on the basis of the expected composition.

The products obtained by the sodium hydroxide method were compared with those obtained by sodium peroxide method. The benzaldehyde and the *o*-and *p*-hydroxybenzaldehydes gave their respective acids in quantity more than the chalkones by sodium peroxide condensation. This is due to the easy oxidation of the aldehydes in presence of hydroxy group.

Chalkone Dibromides (III).—To the solution of the corresponding chalkone (0.01*M*) in chloroform (10c.c.) was added a 25% solution of bromine (0.01*M*) in chloroform. The mixture was kept for 2 hours when a solid separated which was filtered; yield 0.007-0.01 g. The following compounds were prepared:

(*i*) $R_1=R_2=R_3=H$, m.p. 158°.
(*ii*) $R_1=OMe$, $R_2=R_3=H$,m.p. 150°.
(*iii*) $R_3=OH$, $R_1=R_2=H$,m.p. 190°.
(*iv*) $R_2=OH$, $R_1=R_3=H$,m.p. 140°.
(*v*) $R_1=OH$,$R_2=R_3=H$,m.p. 170°.

Percentage of bromine is in accord with the value calculated on the basis of the expected composition.

Flavones (IV).—The chalkone dibromide (1 g.), suspended in ethanol (10c.c.), was treated with 2*N*-NaOH (5c.c.) solution. After 2 hrs. the crude mass was filtered and crystallised from acetic acid; yield 0.4-0.6.g. The following compounds were prepared:

(*i*) $R_1=R_2=R_3=H$,m.p. 226°.
(*ii*) $R_1=OMe$, $R_2=R_3=H$,m.p. 228°.
(*iii*) $R_3=OH$,$R_1=R_2=H$,m.p. 210°.
(*iv*) $R_2=OH$,$R_1=R_3=H$,m.p. 234°.
(*v*) $R_1=OH$, $R_2=R_3=H$,m.p. 240°.

The analytical data are in accord with those calculated on the expected composition.

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Substituted 12-Aminobenz/b/Acridines

A. K. Chatterjee

The synthesis of substitutd 7-aminobenz/c/acridines as potential amoebacides has been reported by Elslager *et al.* (*J. Amer. Chem. Soc.*, 1957, **79**, 4699; 1958, **80**, 451) and by Short *et al.* (*ibid.*, 1958, **80**, 223). Chatterjee (*J. Org. Chem.*, 1959, **24**, 856, 2067) reported the preparation of a few substituted 12-aminobenz/a/acridines and 7-aminobenz/c/-acridines as potential amoebacides. The present communication deals with the preparation of some substituted 12-aminobenz/b/acridines for trial on *E. histolytica*.

The compounds were obtained by the action of 12-chlorobenz/b/acridine, prepared from 2-hydroxy-3-naphthoic acid according to Bachman *et al.* (*J. Org. Chem.*, 1948, **13**, 89), on the appropriate amine in phenol (Table I).

TABLE I

No.	Compound.	Formula.	M.P.	%Carbon.		%Hydrogen.	
				Found.	Calc.	Found.	Calc.
1	12-*p*-Chloroanilinobenz/b/A	$C_{23}H_{15}N_2Cl$	254°	77.69	77.86	3.80	4.23
2	12-*m*-Chloroanilinobenz/b/A	$C_{23}H_{15}N_2Cl$	210°	78.10	77.86	4.20	4.23
3	12-*p*-Bromoanilinobenz/b/A	$C_{23}H_{15}N_2Br$	260°	69.26	69.17	3.56	3.76
4	12-*m*-Bromoanilinobenz/b/A	$C_{23}H_{15}N_2Br$	203°	69.10	69.17	3.43	3.76
5	12-*p*-Anisidinobenz/b/A	$C_{24}H_{18}ON_2$	213°	82.44	82.29	4.78	5.14
6	12-*p*-Toluidinobenz/b/A	$C_{24}H_{18}N_2$	210°	86.33	86.23	5.00	5.39
7	12-*m*-Toluidinobenz/b/A	$C_{24}H_{18}N_2$	202°	85.99	86.23	4.92	5.39
8	12-Anilinobenz/b/A	$C_{23}H_{16}N_2$	228°	85.94	86.25	4.76	5.00
9	12-(8′-Quinolyl) aminobenz/b/A	$C_{26}H_{17}N_3$	278°	84.44	84.10	4.58	4.58
10	12-(6′-Chloro-8′-quinolyl)-aminobenz/b/A	$C_{26}H_{16}N_3Cl$	294°	77.14	76.94	3.69	3.95
11	12-(2′-Phenoxyethyl)-aminobenz/b/A-S	$C_{25}H_{20}ON_2, C_7H_6O_3$	205°	76.75	76.49	4.91	5.18
12	12-(3′-Phenoxypropyl)-aminobenz/b/A-S	$C_{26}H_{22}ON_2, C_7H_6O_3$	211°	76.94	76.74	5.05	5.43
13	12-(1′Naphthyl)-aminobenz/b/A-S	$C_{27}H_{18}N_2$, $C_7H_6O_3$	212°	80.25	80.31	4.44	4.72
14	12-(2′-Naphthyl)-aminobenz/b/A-S	$C_{27}H_{18}N_2$, $C_7H_6O_3$	232°	80.11	80.31	4.69	4.72

N.B.—A stands for acridine and S for salicylate.

General Method of Preparation.—12-Chlorobenz/b/acridine (0.005*M*) was dissolved in freshly distilled phenol (15c.c.) by heating on steam and a slight excess of the appropriate amine added. The mixture was kept at 120° for 2 hours and then poured into an excess of a solution of KOH in water. The base was filtered, washed with water, dried, and purified by crystallisation from benzene, followed by a second crystallisation from 90% ethanol.

In the case of the compounds No. 11 to 14 (Table I), the bases are highly soluble in common solvents. These were extracted with ether and the extract treated with a solution of salicylic acid in ether. After keeping for a few hours, the salicylate was filtered, washed with ether, and crystallised from 90% ethanol.

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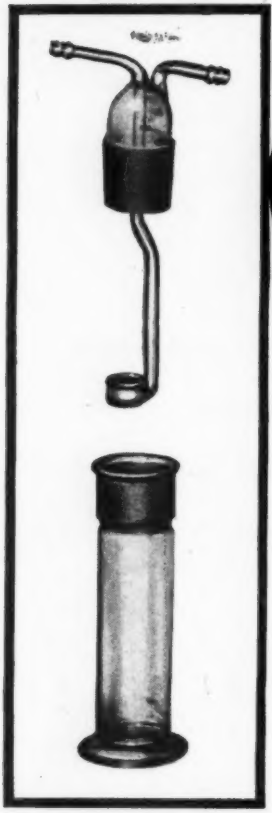

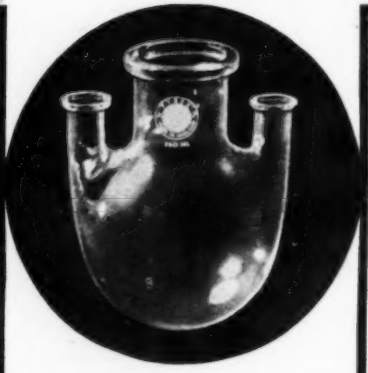

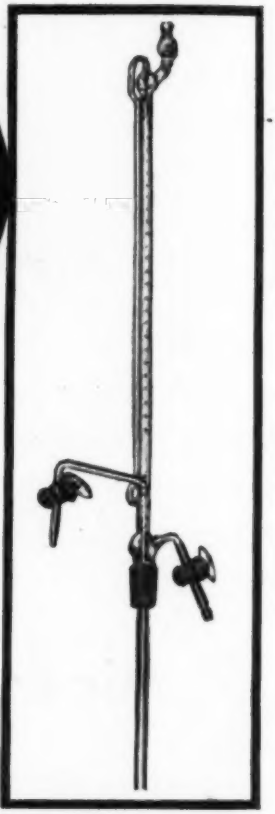

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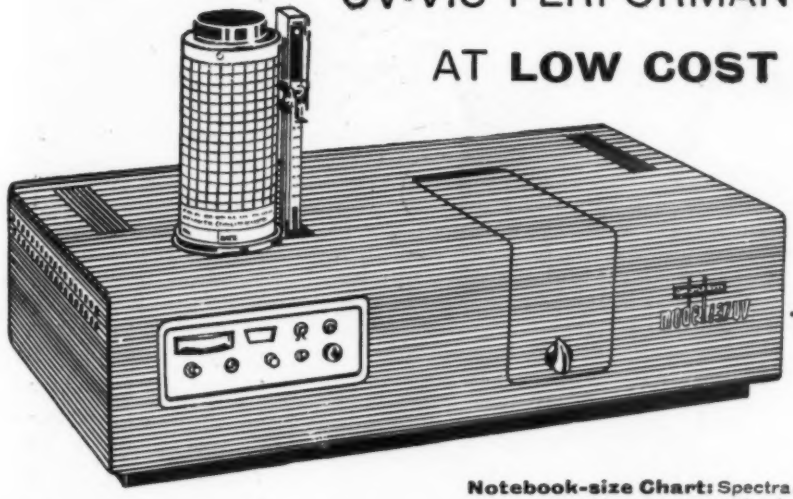

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